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COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT

LEIDEN.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 109—120.
SUPPLEMENT No. 20.
MARCH 1909—APRIL 1911.

* * *

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CONTENTS.

109*a*. **J. P. DALTON**. Researches on the Joule-Kelvin effect, especially at low temperatures. I. Calculations for hydrogen (with a plate).
(*Versl. Kon. Akad.* Maart 1909).

109*b*. **H. KAMERLINGH ONNES**. Methods and apparatus used in the cryogenic laboratory. XV. An apparatus for the purification of gaseous hydrogen by means of liquid hydrogen (with a plate).
(*Versl. Kon. Akad.* Maart 1909).

109*c*. **J. P. DALTON**. Researches on the Joule-Kelvin effect, especially at low temperatures. II. The Joule-Kelvin effect for air at 0° C. and at pressures up to 42 atmospheres (with two plates).
(*Versl. Kon. Akad.* April 1909).

110. **HENRI and JEAN BECQUEREL and H. KAMERLINGH ONNES**. On phosphorescence at very low temperatures (with two plates).
(*Versl. Kon. Akad.* April 1909).

111. **P. LENARD, H. KAMERLINGH ONNES and W. E. PAULI**. The behaviour of the phosphorescent sulphides of

351176

the alkaline earths at various temperatures, and particularly at very low temperatures (with a plate).
(*Versl. Kon. Akad.* Juni 1909).

112. **H. KAMERLINGH ONNES.** Isotherms of monatomic gases and their binary mixtures III. Data concerning neon and helium.
(*Versl. Kon. Akad.* Juni 1909).

113. **ERNST COHEN and J. OLIE Jr.** The atomic volume of allotropic modifications at very low temperatures (with a plate).
(*Versl. Kon. Akad.* October 1909).

114. **PIERRE WEISS and H. KAMERLINGH ONNES.** Researches on magnetization at very low temperatures (with two plates).
(*Versl. Kon Akad.* Februari 1910).

115. **C A. CROMMELIN.** Isotherms of monatomic gases and of their binary mixtures. IV. Remarks on the preparation of argon. V. Vapour pressures above — 140° C., critical temperature and critical pressure of argon (with a plate).
(*Versl. Kon. Akad.* April 1910).

116. **H. KAMERLINGH ONNES and ALBERT PERRIER.** Researches on the magnetization of liquid and solid oxygen (with a plate).
(*Versl. Kon. Akad.* April 1910).

117. **E. MATHIAS and H. KAMERLINGH ONNES.** The rectilinear diameter for oxygen (with three plates).
(*Versl. Kon. Akad.* Januari 1911).

118*a*. **C. A. CROMMELIN**. Isotherms of monatomic gases and of their binary mixtures VI. Coexisting liquid and vapour densities of argon; calculation of the critical density of argon (with a plate).
(*Versl. Kon. Akad.* September 1910).

118*b*. **H. KAMERLINGH ONNES and C. A. CROMMELIN**. Isotherms of monatomic gases and of their binary mixtures VII. Isotherms of argon between + 20° C. and — 150° C (with three plates).
(*Versl. Kon. Akad.* October 1910).

119. **H. KAMERLINGH ONNES**. Further experiments with liquid helium. A Isotherms of monatomic gases etc. VIII. Thermal properties of helium. B. On the change in the resistance of pure metals at very low temperatures etc. III. The resistance of platinum at helium temperatures (with three plates).
(*Versl. Kon. Akad.* Februari 1911).

120*a*. **H. KAMERLINGH ONNES and C. A. CROMMELIN**. Isotherms of monatomic substances and of their binary mixtures. IX. The behaviour of argon with regard to the law of corresponding states (with a plate).
(*Versl. Kon. Akad.* Februari 1911).

120*b*. **H. KAMERLINGH ONNES**. Further experiments with liquid helium. C. On the change of electric resistance of pure metals at very low temperatures etc. IV. The resistance of pure mercury at helium temperatures.
(*Versl. Kon. Akad.* April 1911).

SUPPLEMENT.

20. **JEAN BECQUEREL.** Contribution à la connaissance du phénomène de ZEEMAN dans les cristaux (with a plate).
(*Versl. Kon. Akad.* Juni 1909).

For insertion in Volume N^0. **109–120**.

Errata Communication N^0. 115.

p. 12 formula (4) for "$\frac{\partial^2\pi}{\partial\omega\,\partial\pi}$" read "$\frac{\partial^2\pi}{\partial\omega\,\partial\tau}$".

p. 14 l. 4 from the bottom: for "147" read "47".

Errata Communication N^0. 116.

p. 28 l. 1 from the bottom: after 275.6 insert $\times 10^{-6}$.
p. 29 l. 14 „ „ „ „ 330.0 „ $\times 10^{-6}$.

Errata Communication N^0. 117.

p. 9 l. 2 from the bottom: for "corrsspondants" read "correspondants".
l. 1 from the bottom: for "Toulouss" read "Toulouse".

Errata Communication N^0. 118a.

p. 3 l. 15 from the top: for "waterbad" read "waterbath".
p. 4 l. 12 „ „ „ „ "1 and 2" read "liq and vap".
p. 9 l. 3 „ „ „ „ "Bij" read "By".

Erratum Communication N^0. 118b.

p. 24 l. 16 from the top: for ".107545" read "1.07545".

Erratum Communication N^0. 120a.

p. 9 l. 14 from the bottom: for "122.21" read "121.21".

Errata Communication N⁰. 109*a*.

Title-page line 1 from the bottom: for 1057—1067 read 924—934,

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

Director of the Laboratory.

No. 109a.

J. P. DALTON, M.A., B.Sc., CARNEGIE Research Fellow. "Researches on the JOULE-KELVIN effect, especially at low temperatures. I. Calculations for hydrogen." (*With a plate.*)

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam*, **27 Maart 1909**, pp. 1057—1067.)

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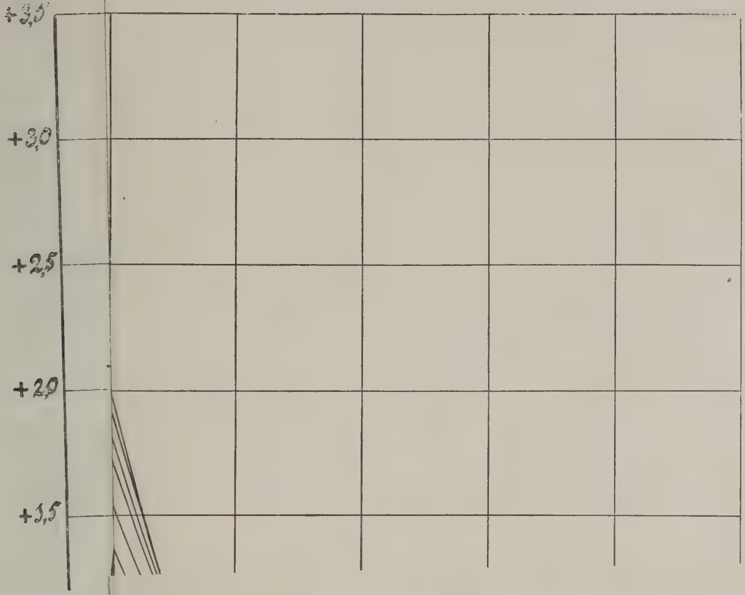
J. n''.



J. P. DALTON. "Researches on the Joule-Kelvin-effect particularly at low temperatures. I. Calculations for hydrogen".

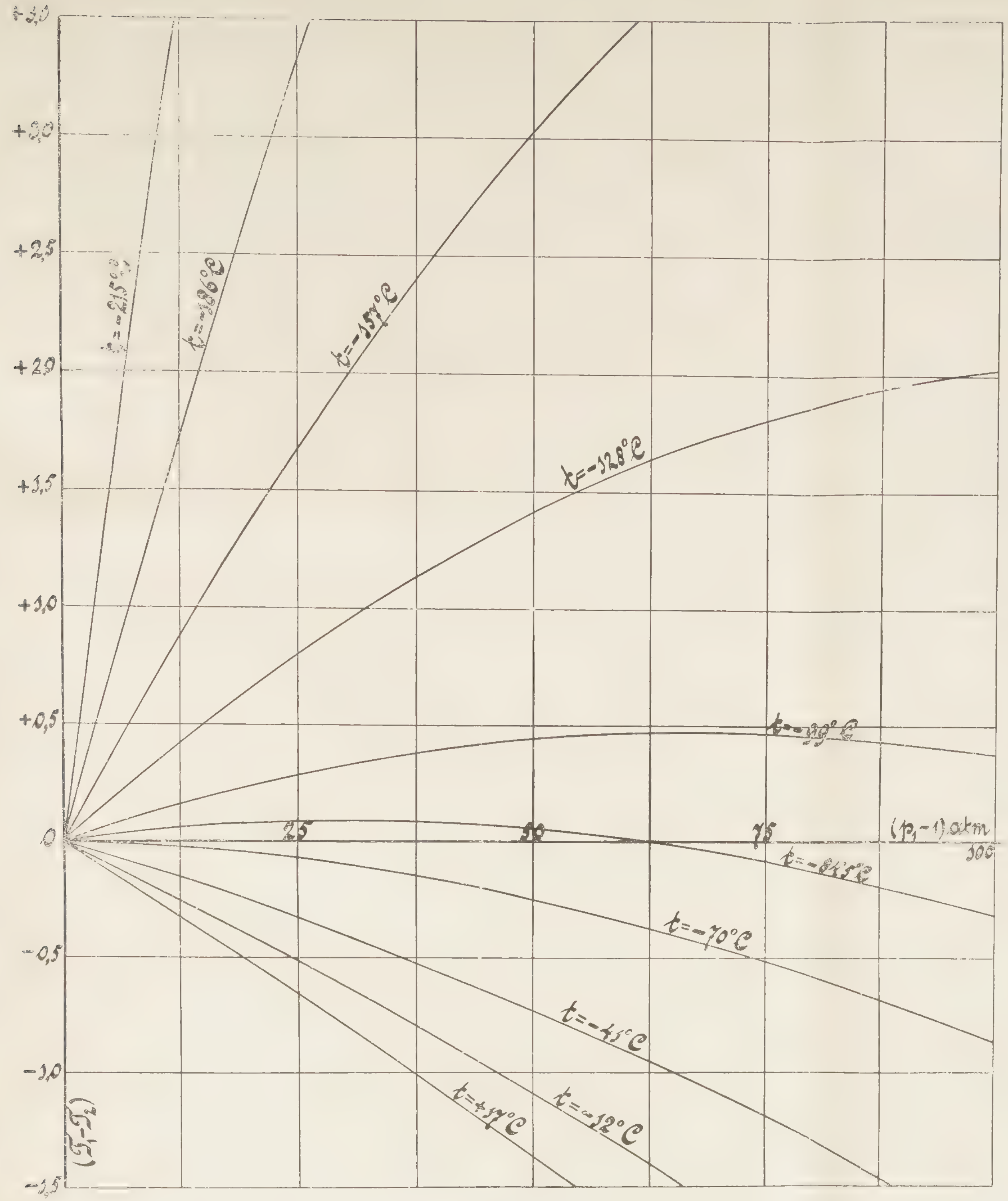


Fig. 1.

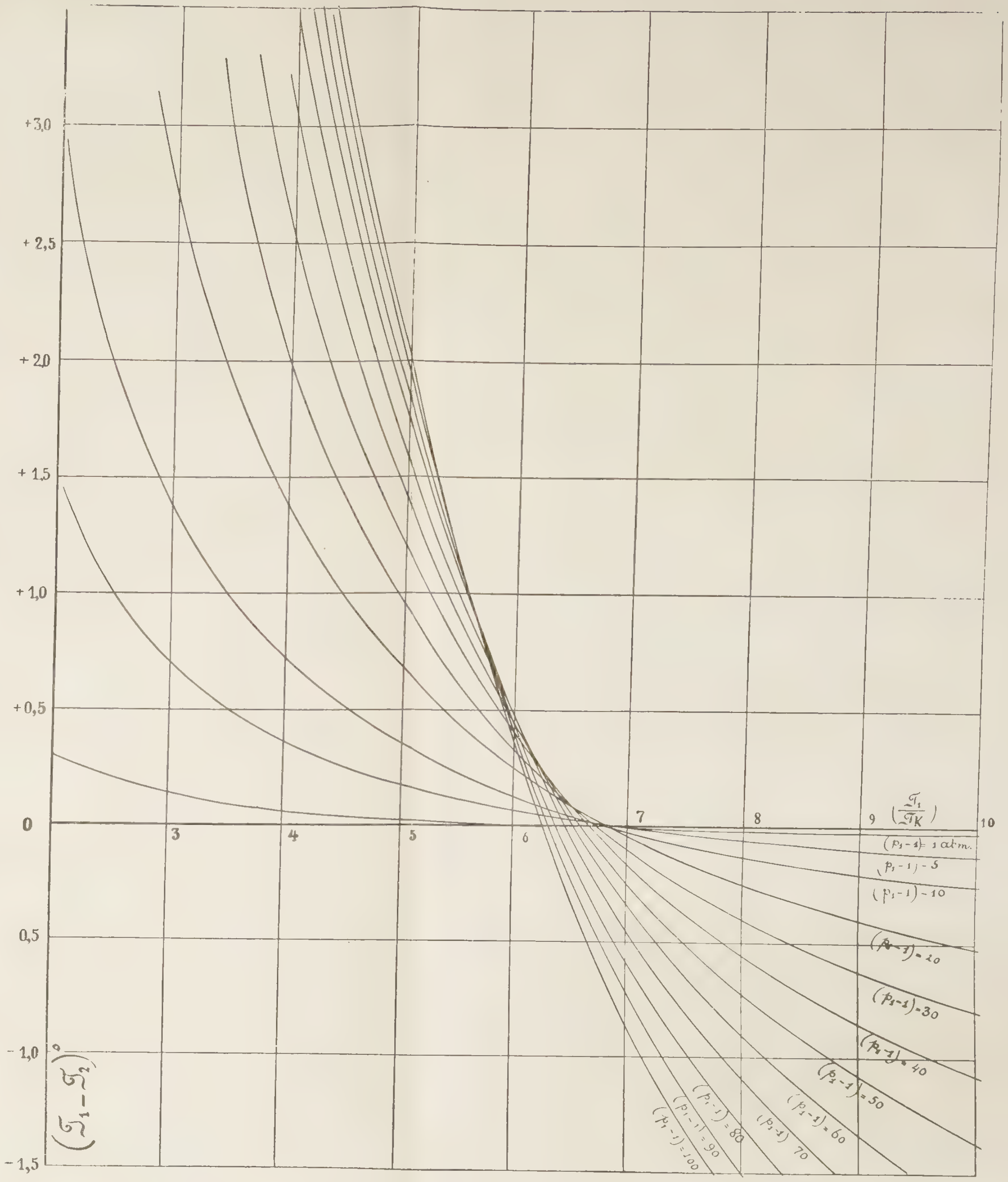


Fig. 2.

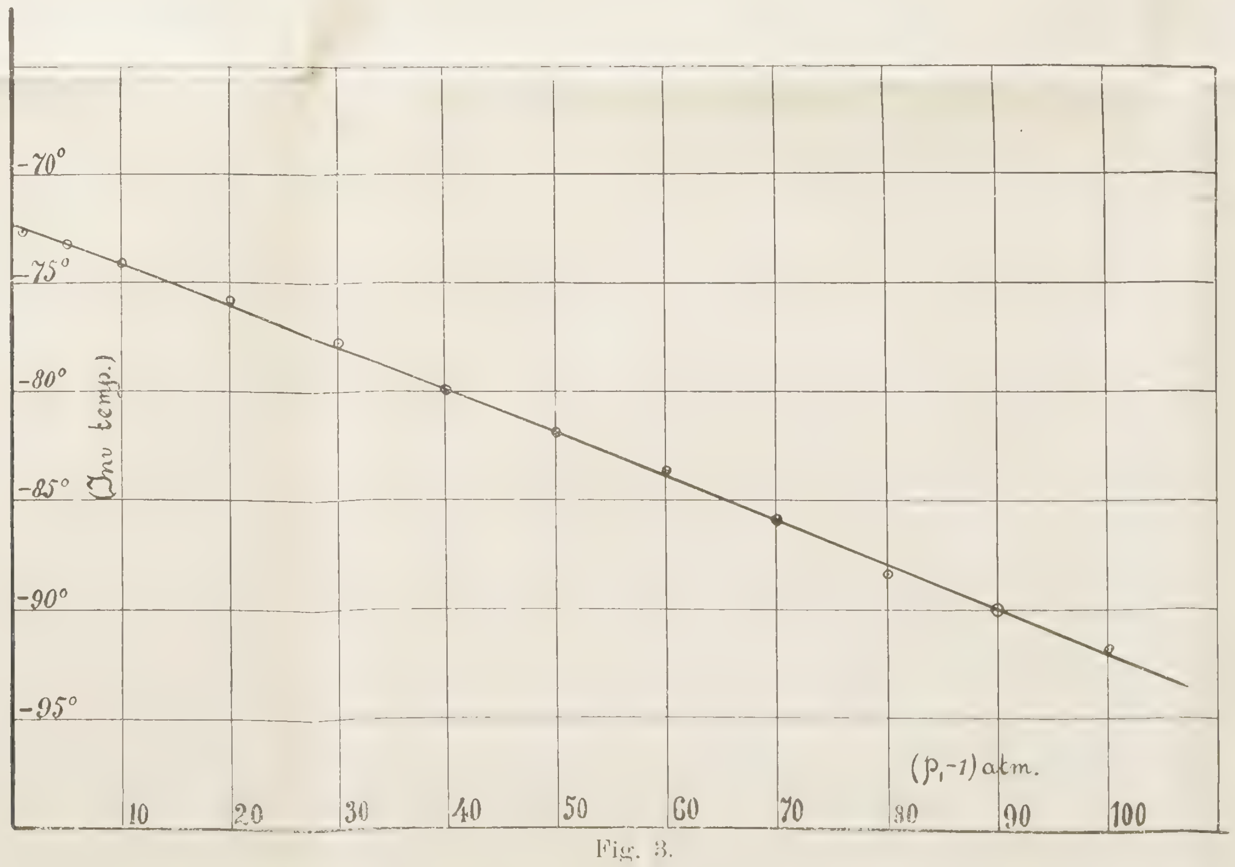


Fig. 3.

Communication No. 109a.

J. P. DALTON, M.A., B.Sc., CARNEGIE Research Fellow.
"*Researches on the* JOULE-KELVIN *effect, especially at low temperatures.* I. *Calculations for hydrogen*".

§ 1. The present calculations form part of a research which was undertaken [1]) with a view to devising an apparatus for determining the JOULE-KELVIN-effect obtained in expanding helium at the temperature of liquid hydrogen, and thus to lead to some decision regarding the possibility of liquefying helium — an open question at that time. To test the apparatus, expansion experiments were first to be made with air at ordinary temperature, and with hydrogen at the temperature of liquid oxygen; but in the construction of the apparatus it had always to be kept in view that it was eventually to be used in liquid hydrogen. Preliminary experiments showed that the apparatus in its original form did not give a true JOULE-KELVIN-effect, and thus led to a special investigation of the thermodynamics of expansion through a valve and how a valve apparatus has to be arranged so that the *enthalpy* [2]) before and after expansion remains the same. The results of this investigation will be published in this and following communications, for they lose none of their interest by the circumstance that the original object of the research has been disposed of by the liquefaction of helium [3]).

§ 2. Since the experiments of JOULE and KELVIN [4]) of 50 years ago very little experimental work upon similar expansions of gases

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1) The beginning of the research was already referred to in Comm. No. 108.

2) This name has been suggested by KAMERLINGH ONNES to indicate the function $(\varepsilon + pv)$ — the "Heat function" of GIBBS. H. L. CALLENDAR (Phil. Mag. [6]. 5. p. 48. (1903).) calls this expansion "Adiathermal".

3) H. KAMERLINGH ONNES: Comm. No. 108.

4) JOULE and KELVIN: Phil. Mag. [4]. 4. p. 481. (1852); Phil. Trans 143. p. 357. (1853); 144. p. 321. (1854); 152. p. 579. (1862).

has been published. This lack of confirmation is rather surprising when we consider the importance of the JOULE-KELVIN experiments in gas-thermometry and the frequency with which their results are employed in various theoretical thermodynamical investigations. With the exception of some rough experiments by REGNAULT [1]) upon various gases, and the work of E. NATANSON [2]) and KESTER [3]) upon CO_2, no further measurements of the JOULE-KELVIN-effect seem to have been made. REGNAULT did not obtain results sufficiently definite to lead to any theoretical conclusions, and the results obtained by the other experimenters are not in agreement.

§ 3. Although JOULE and KELVIN began their experiments by allowing the expansion to take place through a small aperture, they soon abandoned that form of apparatus, and used instead a porous plug so as to ensure, by friction in the plug, the immediate conversion into heat of the energy generated, and also to ensure that the expanded gas should issue in a "quiet tranquil stream without jets or rapids". (See § 6, note 1). NATANSON and KESTER also used a porous plug.

More recently OLSZEWSKI has determined "inversion-points" for various gases, and has returned to the original reduction-valve form of apparatus; but while JOULE and KELVIN's highest initial pressure was not greater than 6 atmospheres, OLSZEWSKI expanded from considerably higher pressures. Since the apparatus to be used in my research resembled that used by OLSZEWSKI, a careful examination of his experimental results and of the criticisms concerning them which have been published was necessary.

§ 4. OLSZEWSKI's first determination [4]) was of an "inversion-point" for hydrogen. This result was subsequently used by POR-

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1) V. REGNAULT: C. R. 69. p. 780 (1869).
2) E. NATANSON: Wied. Ann. 31. p. 502 (1887).
3) F. E. KESTER: Phys. Zeits. 6. p. 44 (1905).
Phys. Rev. 21. p. 260 (1905).
4) K. OLSZEWSKI: Phil. Mag. [6]. 3. p. 535. (1902).
Ann. Phys. 7. p. 818. (1902).

TER [1]) as a means of discriminating between the validity of certain equations of state. Later OLSZEWSKI investigated [2]) the dependence of inversion temperature upon initial pressure in the case of air and nitrogen, and found that inversion temperature decreased with falling initial pressure. The results of this research have been criticised in a theoretical investigation recently published by HAMILTON DICKSON. [3]) DICKSON reached the conclusion that OLSZEWSKI's experiment differs fundamentally from that of JOULE and KELVIN. This difference he attributed to the different kinetic energies possessed by the gas in the OLSZEWSKI experiment before and after expansion. It will be shown in a subsequent paper that conduction of heat and loss of pressure in OLSZEWSKI's experiments are probably much more important factors in the result than the change of kinetic energy.

§ 5. DICKSON's criticism was based upon calculations made from VAN DER WAALS's equation of state, but, as this equation is not quantitatively correct, the results obtained are of doubtful value. But if we calculate from the real isothermals of the experimental gas, we ought to obtain close correspondence between the calculated and experimental values of the JOULE-KELVIN effect, in so far as no uncertainty is introduced by errors in the experimental data. To effect such calculations KAMERLINGH ONNES [4]) has given empirical equations of state, which, if specialised for the experimental gas, and, if necessary, between definite limits of temperature and pressure, represent the actual isotherms of the gas to the limits of accuracy of the observations, and in a form easy to manipulate. In this equation the product pv is expressed as a series of five powers of the density; thus

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} + \frac{E}{v^6} + \frac{E}{v^8} \quad . \quad . \quad . \quad . \; (2)$$

where p is expressed in atmospheres, v in terms of the theoretical normal volume as unit, and the "virial-coefficients" $A, B, C.$ etc.,

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1) A. W. PORTER: Phil. Mag. [6]. 11. p. 554 (1906).

2) K. OLSZEWSKI: Phil. Mag. [6]. 13. p. 723 (1907).

3) J. D. HAMILTON DICKSON: Phil. Mag [6]. 15. p. 126. (1908).

4) H. KAMERLINGH ONNES: Comm. Nos. 71 and 74.

are calculated as functions of the temperature from the experimental isotherms of the gas in question, in conjunction with the isotherms of other substances which are brought into relation with the one investigated by means of the law of corresponding states. On this account the equation is usually given in the so-called reduced form :

$$\lambda \mathfrak{p}\mathfrak{v} = \mathfrak{A} + \frac{\mathfrak{B}}{\lambda \mathfrak{v}} + \frac{\mathfrak{C}}{\lambda^2 \mathfrak{v}^2} + \frac{\mathfrak{D}}{\lambda^4 \mathfrak{v}^4} + \frac{\mathfrak{E}}{\lambda^6 \mathfrak{v}^6} + \frac{\mathfrak{F}}{\lambda^8 \mathfrak{v}^8} \quad . \quad . \quad . \quad (2)$$

were λ is equal to $\frac{T_k}{p_k v_k} \cdot$ $\mathfrak{p}$ and $\mathfrak{v}$ the reduced pressures and volumes respectively, and

$$\mathfrak{A} = \frac{A}{T_k}\, ; \; \mathfrak{B} = \frac{B}{T_k^{\,2}} p_k\, ; \; \mathfrak{C} = \frac{C}{T_k^{\,3}} p_k^{\,2}; \text{ etc.}$$

§ 6. If the two following experimental conditions are fulfilled, viz. :

1. that the difference between the kinetic energies of the gas before and after expansion is negligible ; and
2. that the conduction of heat from the apparatus to the expanding gas is also negligible ;

then the expansion process will be represented by the equation

$$\varepsilon_1 + p_1 v_1 = \varepsilon_2 + p_2 v_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(where $\varepsilon =$ internal energy of the gas, and the subscripts 1 and 2 refer to the initial and final states respectively) quite independently of whether the expansion has taken place through a valve or a plug 1)), or from a high or low initial pressure. Equation (3) representing an expansion which is characterised by equal values of enthalpy in the initial and final states may by the usual methods 2)) be transformed into

---

1) In expansion through a valve, since in parts of the jet the kinetic energy temporarily reaches values which are not negligible, intermediate stages of the process are not characterised by equal values of the enthalpy ; in expansion through a plug the process, if it agrees with the theoretical suppositions, becomes *isenthalpic*.

2) See : J. P. KUENEN : Die Zustandsgleichung, pp. 106—9. Braunschweig. 1907.

p. 6 line 8 from the top: for "were" read "where".

$$\overline{C_v}\,(T_1 - T_2) = \int_{v_1}^{v_2} \left[T \left(\frac{\partial p}{\partial T}\right)_v - p \right] dv + p_2 v_2 - p_1 v_1 \quad . \; . \; . \tag{4}$$

or

$$\overline{C_p}\,(T_1 - T_2) = - \int_{p_1}^{p_2} \left[T \left(\frac{\partial v}{\partial T}\right)_p - v \right] dp \quad . \; . \; . \; . \; . \; . \; . \tag{5}$$

where

$$\overline{C}\,(T_1 - T_2) = \int_{T_2}^{T_1} C \, dT.$$

Since T_1 and T_2 never differ much in value, and since, in any case, C varies very slowly with temperature, the difference between $\overline{C}$ and C must be extremely small.

For the present calculation equation (4) seems at first sight more directly applicable than (5), but the evaluation of v_2 would necessitate the use of successive approximations; it is, therefore, better to use equation (5). For this purpose, the following transformation, valid as long as excessive densities are not reached, may be applied to equation (2); this equation may be written in terms of reduced pressure as

$$\lambda\, \mathfrak{p}\mathfrak{v} = \mathfrak{A}^{(p)} + \mathfrak{B}^{(p)}\, \mathfrak{p} + \mathfrak{C}^{(p)}\, \mathfrak{p}^2 + \mathfrak{D}^{(p)}\, \mathfrak{p}^3 + \mathfrak{E}^{(p)}\, \mathfrak{p}^4 + etc \quad . \; . \tag{6}$$

if

$$\mathfrak{A}^{(p)} = \mathfrak{A} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \tag{7}$$

$$\mathfrak{B}^{(p)} = \frac{\mathfrak{B}}{\mathfrak{A}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \tag{8}$$

$$\mathfrak{C}^{(p)} = \frac{\mathfrak{C}\,\mathfrak{A} - \mathfrak{B}^2}{\mathfrak{A}^3} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \tag{9}$$

$$\mathfrak{D}^{(p)} = \frac{2\mathfrak{B}^3 - 3\,\mathfrak{A}\mathfrak{B}\mathfrak{C}}{\mathfrak{A}^5} \quad . \; . \; . \; . \; . \; . \; . \tag{10}$$

$$\mathfrak{E}^{(p)} = \frac{\mathfrak{D}\mathfrak{A}^3 - 5\,\mathfrak{B}^4 - 2\,\mathfrak{A}^2\mathfrak{C}^2 + 10\,\mathfrak{A}\mathfrak{B}^2\mathfrak{C}}{\mathfrak{A}^7} \quad . \tag{11}$$

Equation (5) in reduced magnitudes becomes

$$\overline{C}_p (T_1 - T_2) = - T_k \lambda \int_{\mathfrak{p}_1}^{\mathfrak{p}_2} \left[\mathfrak{t} \left(\frac{\partial \mathfrak{v}}{\partial \mathfrak{t}} \right)_{\mathfrak{p}} - \mathfrak{v} \right] d\mathfrak{p} \quad . \; . \; . \; . \quad (12)$$

Since

$$\mathfrak{t} \frac{d\mathfrak{A}}{d\mathfrak{t}} - \mathfrak{A} = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

equations (12) and (6) give the relation

$$\begin{aligned} \overline{C}_p (T_1 - T_2) = {} & \frac{T_k}{p_k} \left(\mathfrak{t} \frac{d\mathfrak{B}^{(p)}}{d\mathfrak{t}} - \mathfrak{B}^{(p)} \right) (p_1 - p_2) + \\ & \frac{T_k}{2p_k^2} \left(\mathfrak{t} \frac{d\mathfrak{C}^{(p)}}{d\mathfrak{t}} - \mathfrak{C}^{(p)} \right) (p_1^2 - p_2^2) + \\ & \frac{T_k}{3p_k^3} \left(\mathfrak{t} \frac{d\mathfrak{D}^{(p)}}{d\mathfrak{t}} - \mathfrak{D}^{(p)} \right) (p_1^3 - p_2^3) + \text{etc.} \quad . \; . \quad (14) \end{aligned}$$

Hence, if we return to the original coefficients by means of (8), (9), (10), (11) and (13), we obtain an expression for the heat-effect in terms of the virial-coefficients, and the initial and final pressures; and if the expansion takes place against atmospheric pressure, this relation becomes

$$\begin{aligned} (T_1 - T_2) = {} & \frac{\mathfrak{t} \frac{d\mathfrak{B}}{d\mathfrak{t}} - 2\mathfrak{B}}{\mathfrak{A}} \cdot \frac{T_k}{\overline{C}_p p_k} (p_1 - 1) + \\ & + \frac{\mathfrak{A} \left(\mathfrak{t} \frac{d\mathfrak{C}}{d\mathfrak{t}} - 3\mathfrak{C} \right) - 2\mathfrak{B} \left(\mathfrak{t} \frac{d\mathfrak{B}}{d\mathfrak{t}} - 2\mathfrak{B} \right)}{2\mathfrak{A}^3 p_k} \frac{T_k}{\overline{C}_p p_k} (p_1^2 - 1) + \\ & + \frac{3 \left(\mathfrak{t} \frac{d\mathfrak{B}}{d\mathfrak{t}} - 2\mathfrak{B} \right) (2\mathfrak{B}^2 - \mathfrak{A}\mathfrak{C}) - 3\mathfrak{A}\mathfrak{B} \left(\mathfrak{t} \frac{d\mathfrak{C}}{d\mathfrak{t}} - 3\mathfrak{C} \right)}{3\mathfrak{A}^5 p_k^2} \frac{T_k}{\overline{C}_p p_k} (p_1^3 - 1) + \\ & + \frac{20 \left(\mathfrak{t} \frac{d\mathfrak{B}}{d\mathfrak{t}} - 2\mathfrak{B} \right) (\mathfrak{A}\mathfrak{B}\mathfrak{C} - \mathfrak{B}^3) + \left(\mathfrak{t} \frac{d\mathfrak{C}}{d\mathfrak{t}} - 3\mathfrak{C} \right) (10\mathfrak{A}\mathfrak{B}^2 - 4\mathfrak{A}^2\mathfrak{C}) + \mathfrak{A}^3 \left(\mathfrak{t} \frac{d\mathfrak{D}}{d\mathfrak{t}} - 5\mathfrak{D} \right)}{4\mathfrak{A}^7 p_k^3} \\ & \frac{T_k}{\overline{C}_p p_k} (p_1^4 - 1) + \text{etc.} \quad . \; . \; . \quad (15) \end{aligned}$$

which is the equation to be used in calculating the heat-effects

§ 7. As a first example I have taken hydrogen, and from equation (15) have calculated the heat effects produced when hydrogen is expanded against atmospheric pressure under various conditions of initial temperature and pressure. The values of the virial-coefficients, specialised to fit the isotherms of KAMERLINGH ONNES and BRAAK [1]) down to —217° C. and not yet published, were kindly placed at my disposal by Professor ONNES. These coefficients are

$$\left.\begin{aligned}\mathfrak{A} &= 0.0036618\,\mathfrak{t}\\ 10^{8}\,\mathfrak{B} &= 168.982\,\mathfrak{t} - 435.381 - 722.848\frac{1}{\mathfrak{t}} + \\ &\qquad + 420.696\frac{1}{\mathfrak{t}^{3}} - 118.456\frac{1}{\mathfrak{t}^{5}}\\ 10^{11}\,\mathfrak{C} &= 50.3923\,\mathfrak{t} + 131.386 + 131.2531\frac{1}{\mathfrak{t}} + \\ &\qquad + 199.2748\frac{1}{\mathfrak{t}^{3}} - 50.6347\frac{1}{\mathfrak{t}^{5}}\\ 10^{18}\,\mathfrak{D} &= 434.680\,\mathfrak{t} - 131.462 - 903.004\frac{1}{\mathfrak{t}} + \\ &\qquad + 367.7055\frac{1}{\mathfrak{t}^{3}} - 178.5625\frac{1}{\mathfrak{t}^{5}}\end{aligned}\right\rbrace (16)$$

The values of the critical constants used in the reduction were $p_k = 15$ atm. and $T_k = 29°$ abs.; but as the reduction is ultimately reversed the accuracy or otherwise of these constants is immaterial. The WIEDEMANN value of $\overline{C_p} = 3.41$ cal. has been used. An estimate of the change of $\overline{C_p}$ with temperature was obtained by combining equation (2) with the well-known thermodynamical relation

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p . \quad . \quad . \quad . \quad . \quad . \qquad (17)$$

and regarding C_v as independent of the temperature [2]). This

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1) H. KAMERLINGH ONNES and C. BRAAK: Comm. No's 97*a*, 99*a*, 100.

2) Cf. A. W. WITKOWSKI: Bull. de l'Acad. d. Sciences de Crac. Oct.-Nov. 1895.

The comparatively great change of C_v and C_p with temperature deduced by

TABLE I.

t =	10	9	8	7	6.5	6	5	4	3	2
T_{abs} =	290	261	232	203	188.5	174	145	116	87	58
$t°C$ =	+ 17	— 12	— 41	— 70	— 84.5	— 99	— 128	— 157	— 186	— 215
$(p_1 - 1)$ atm.					$T_1 - T_2$					
1	— 0.026	— 0.019	— 0.011	— 0.001	+ 0.006	+ 0.015	+ 0.037	+ 0.073	+ 0.141	+ 0.291
5	— 0.128	— 0.098	— 0.059	— 0.006	+ 0.028	+ 0.071	+ 0.180	+ 0.361	+ 0.698	+ 1.466
10	— 0.259	— 0.198	— 0.121	— 0.016	+ 0.051	+ 0.135	+ 0.351	+ 0.711	+ 1.382	+ 2.951
20	— 0.526	— 0.407	— 0.254	— 0.049	+ 0.081	+ 0.247	+ 0.668	+ 1.371	+ 2.694	+ 5.957
30	— 0.799	— 0.625	— 0.400	— 0.100	+ 0.092	+ 0.335	+ 0.951	+ 1.991	+ 3.931	
40	— 1.080	— 0.852	— 0.558	— 0.166	+ 0.083	+ 0.400	+ 1.200	+ 2.538	+ 5.073	
50	— 1.367	— 1.088	— 0.729	— 0.249	+ 0.056	+ 0.444	+ 1.418	+ 3.044	+ 6.108	
60	— 1.662	— 1.333	— 0.909	— 0.347	+ 0.011	+ 0.467	+ 1.603	+ 5.497	+ 7.023	
70	— 1.963	— 1.587	— 1.102	— 0.460	— 0.052	+ 0.468	+ 1.757	+ 3.897		
80	— 2.270	— 1.849	— 1.306	— 0.587	— 0.132	+ 0.450	+ 1.881	+ 4.246		
90	— 2.584	— 2.119	— 1.520	— 0.729	— 0.229	+ 0.413	+ 1.976	+ 4.544		
100	— 2.904	— 2.398	— 1.744	— 0.885	— 0.343	+ 0.356	+ 2.043	+ 4.793		

showed that down to —190° C. the variation in C_p at 1 atm. was less than $1\,{}^0/_0$; hence it appeared that a sufficiently high degree of accuracy was reached by retaining the constant value 3.41 throughout these calculations.

For the calculations four terms of equation (2) were found sufficient, for the greatest influence of the $\mathfrak{D}$-term on the values shown in Table I of $T_1 - T_2$ at 100 atm. pressure was not greater than 0°.15. Table I [1]) contains the results of the calculations; from it has been constructed the series of $(T_1 - T_2, p_1 - 1)_{T = const.}$ curves shown in fig. 1, and also the series of $(T_1 - T_2, T_1)_{p_1 = const.}$ curves of fig. 2.

§ 8. Considering the a of his equation as a function of the temperature VAN DER WAALS [2]) deduced the following expression for the JOULE-KELVIN effect:

$$T_1 - T_2 = \frac{2}{mC_p} \times 273 \left[\frac{a}{v_1} \{2\, f(T_1) - T_1 f'(T_1)\} - \frac{RT_1 b}{v_1 - b} \right] \ . \ . \quad (18)$$

and drew attention to the fact that "at a given value of T_1 we may give p_1 such a value that the cooling has a maximum value". The foregoing calculations, the results of which are embodied in Table I, lead to the same conclusion, and show that as the initial pressure increases, the cooling effect (if any) increases, reaches a maximum, diminishes, and finally at high pressures (as long as $\mathfrak{t}_2 > 1$) changes into a heating effect. They show moreover that except in the neighbourhood of temperatures determined by the relation

$$\mathfrak{t}\,\frac{d\mathfrak{B}}{d\mathfrak{t}} - 2\mathfrak{B} = 0 \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (19)$$

or at very high pressures, the subsequent terms of the right-

---

H. LE CHATELIER and E. MALLARD. (Séanc. Soc. de Phys. p. 308. (1888)) from experiments at high temperatures cannot be applied to low temperatures without further investigation.

1) The calculation is not extended beyond the limits of density at each temperature at which powers higher than those occurring in (15) must be taken into account.

2) J. D. VAN DER WAALS. Proc. Kon. Akad. van Wetens. Amsterdam II. p. 379. (1900).

hand member of equation (15) are very small compared with the first, and it is therefore only under these circumstances that the progressive change from cooling to heating could be experimentally realised; but if the critical pressure of the gas is low, as in the case of hydrogen, high reduced pressures are easily attainable, and these changes become of importance. In fact, this warming effect obtained in expansions from high pressure explains the fact that TRAVERS [1]) found hydrogen "a perfect gas down to very low temperatures"; for, in his experiments expansions were made from the comparatively high initial pressure of 200 atm. And in this connection it is also worth remarking that in the liquefaction of helium KAMERLINGH ONNES (loc.cit.) found that if the expansion pressure exceeded a certain value, the expanding gas no longer showed a cooling effect. The curves (fig. 1 and 2) further show that at lower pressures and at temperatures not in the neighbourhood of those defined by equation (19), the cooling effect remains practically proportional to the pressure-difference, and decreases in magnitude as the temperature of the compressed gas is increased. It was under conditions such as these that the JOULE-KELVIN experiments were carried out, and their results embodied in their well-known empirical equation

$$T_1 - T_2 = \frac{A}{T_2}(p_1 - p_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

are in agreement with the foregoing conclusions. The value of A in this equation for hydrogen at + 5° C. was given by JOULE and KELVIN as — 0.03 which is somewhat greater than the above calculated value of — 0,023; but numerical non-correspondence is in this case of no great importance seeing that JOULE and KELVIN's results for hydrogen were very irregular, and the authors declared them to be less trustworthy than those obtained with other gases.

§ 9. With regard to "inversion-points", it is at once evident that the inversion temperature is a function of the initial pressure, and that it does not reach the value $T_{inv} = 7\,T_k$ (see table I).

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[1]) MORRIS W. TRAVERS: Experimental Study of Gases; p. 197 (1901).

p. 12 formula (20): for T_2 in the denominator of the second member read T^2.

From the curves of fig. 2 have been read the following inversion temperatures corresponding with various initial pressures.

TABLE II.

Pressure-difference.	Inversion temperature.
1 atm.	— 72.6° C.
5 „	— 73.2 „
10 „	— 74.1 „
20 „	— 75.8 „
30 „	— 77.8 „
40 „	— 79.9 „
50 „	— 81.9 „
60 „	— 83 6 „
70 „	— 85.9 „
80 „	— 88.3 „
90 „	— 90.0 „
100 „	— 91.7 „

Thus the relation between inversion-temperature and pressure-difference is practically linear (fig. 3), and with increasing initial pressure the inversion temperature falls. If we extrapolate the above table we obtain for a pressure of 115 atm an inversion temperature of — 95° C., where OLSZEWSKI found — 80°.5 C. It is worth noting that NAKAMURA ¹) calculating from REINGANUM's equation of state found a value of — 79° C. for the inversion point; but in his calculation he seems to have taken no account of the influence of initial pressure and his result is valid only for 1 atmosphere.

The results obtained by OLSZEWSKI for air and nitrogen are in marked contrast to those here obtained for hydrogen. The diagrams by which he shows graphically the relation between inversion-temperature and pressure, are lines that are strongly curved, and they exhibit, moreover, an inversion temperature increasing with increasing initial pressure. The calculations given above throw some doubt upon these results. For JOULE and KELVIN found for air at ordinary temperatures a linear relation between cooling-effect and pressure difference; this, compared with the foregoing

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1) S. NAKAMURA: refer. Journ. de Physique (4). 2 p. 704. (1903).

result for hydrogen at — 215° C. renders it highly probable that air and hydrogen follow the law of corresponding states in the JOULE-KELVIN effect, as was to be expected from the facts that their equation of state follows that law, and that both gases are bi-atomic without any chemical complication in the molecule [1]).

Keeping in view this thermodynamic similarity of hydrogen with air or nitrogen it may be inferred from equations (4) or (5) that the inversion temperature curves for all three gases must have the same general properties, and exhibit a relation between inversion temperature and pressure approximately linear; and it can be seen that the small uncertainty in the changes of specific heat with temperature for the different gases cannot account for OLSZEWSKI's finding an opposite effect of initial pressure.

Thus we must conclude that expansion through a reduction-valve of the same construction as that used by OLSZEWSKI does not satisfy the conditions embodied in equations (3) and (15) governing a process at the beginning and end of which the enthalpy has the same value.

A subsequent paper dealing with the experimental portion of this research will show that the cause of this discrepancy can lie in the conditions under which the expansions in OLSZEWSKI's experiments were carried out.

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1) Cf. H. KAMERLINGH ONNES: Comm. No. 23.
DANIEL BERTHELOT: Journ. de Phys. Mars 1903; and
EDGAR BUCKINGHAM: Bull. Bur. Stand. (3). 2. (1907).

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,
Director of the Laboratory.

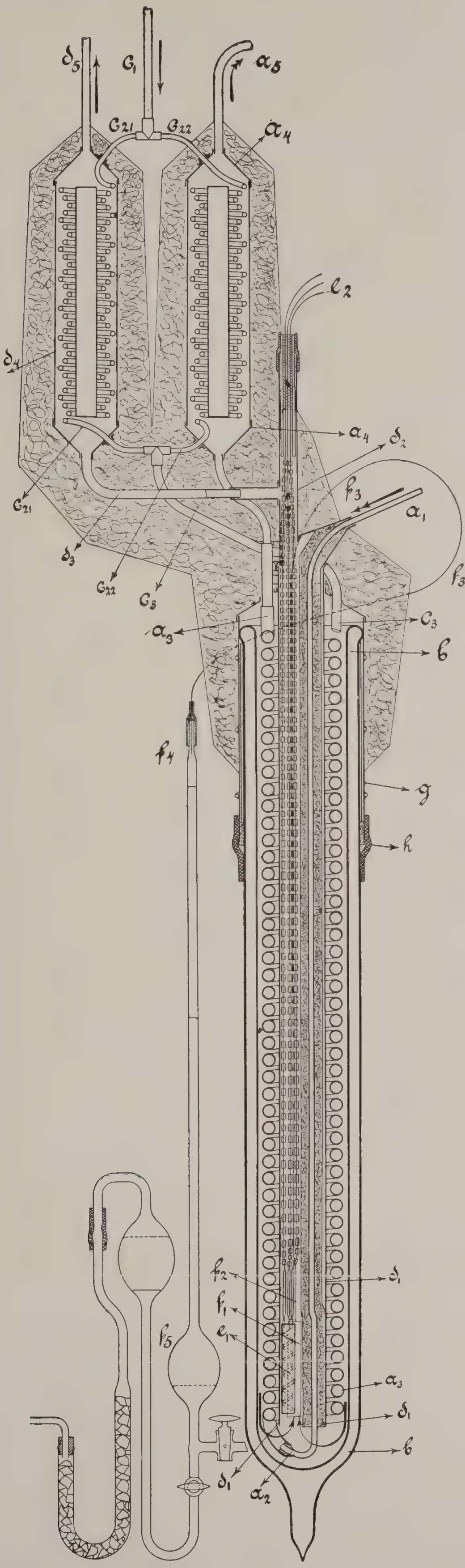
No. 109^b.

Dr. H. KAMERLINGH ONNES. "Methods and apparatus used in the cryogenic laboratory. XV. An apparatus for the purification of gaseous hydrogen by means of liquid hydrogen." (*With a plate*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam*, **27 Máart 1909**, pp. 934—936).

EDUARD IJDO — PRINTER — LEIDEN.

Dr. H. KAMERLINGH ONNES. "Methods and apparatus used in the cryogenic laboratory. XV. An apparatus for the purification of gaseous hydrogen by means of liquid hydrogen".



Communication No. 109b.

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Dr. H. KAMERLINGH ONNES. "*Methods and apparatus used in the cryogenic laboratory.* XV. *An apparatus for the purification of gaseous hydrogen by means of liquid hydrogen*".

In Communication N^0. 94*f* a liquid hydrogen cycle was described, and attention was drawn to the fact that a continuous action of that cycle was possible only when a sufficient quantity of extremely pure hydrogen was available [1]). In section XI of the communication referred to, the method of obtaining this supply was given. The commercial gas was purified by cooling to —205° C. and by means of a liquid-air (oxygen) separator [2]) to such an extent, that, when passed through the hydrogen liquefier it gave some liquid hydrogen (although a comparatively small quantity) before the liquefier became choked, and this liquid, by vaporisation, gave pure hydrogen. When the hydrogen liquefier had again been put in a workable condition, the operations were repeated with a new quantity of gas which had undergone preliminary purification in the liquid-air separator, and the various yields of pure hydrogen thus obtained were carefully collected and united, until the required quantity was available.

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[1]) It can easily be seen that obstruction of the regenerator-spiral must necessarily occur when a little air (or oxygen) is present in the hydrogen. The temperature at different heights of the spiral varies with changes in the velocity of the gas stream, which can scarcely be avoided, and, in any case, occur when the circulation is temporarily stopped. The result of this is that the air is alternately frozen, melted, carried lower down in the spiral and again frozen, until finally the opening of the tube is completely plugged.

[2]) The air separator usually works at a pressure of 60 atm. and with a velocity of 2 M.^{3} per hour; the impurities remaining do not then amount to more than $^1/_4$ $^0/_0$, and the quantity of liquid air used is about 2 litres per hour. In Comm. N^0. 94*e* the value $^1/_{20}$ $^0/_0$ was given: to reach this value, however, the velocity must be much smaller, in order that none of the liquid that separates out should be carried along with the current.

The application of the process to prepare on an industrial scale hydrogen of a degree of purity even greater than that of industrial pure hydrogen starting from lighting gas or yet cheaper from watergas is evident; for laboratory purposes it remains preferable to start from industrial pure hydrogen gas, the cost of it being balanced by the trouble of carying out on a laboratory scale the preparation of hydrogen as pure as industrial pure hydrogen say from lighting gas. If perfectly pure hydrogen is wanted on an industrial scale the process published in the present note can be applied.

This method of operating was rather troublesome, and once I was in possession of a sufficient quantity of pure hydrogen to keep the cycle in continuous action it was an obvious advantage to avail myself of this cycle for the purification of commercial hydrogen. In Suppl. N^0. 18*a* the communication was already made that an apparatus was being constructed, in which the purification of the hydrogen was to be effected by means of its liquefaction, while another apparatus had already been constructed in which the impurities were frozen out of the gaseous hydrogen to be purified, by means of the pure liquid hydrogen of the cycle.

The suitability of the latter apparatus has been proved by long use; it is represented in Pl. I and a description of it is here given.

The chief portion of the apparatus is the spiral a_3, in the lower end of which the liquid hydrogen is vaporised; it is placed in a vacuum vessel b, which is closed by means of a cap g. The hydrogen which is to be purified flows through the tube c_3, between the vacuum glass b, and the cylinder d_1, and along the cooled spiral in the opposite direction to that in which the gaseous hydrogen flows away which is formed by vaporisation inside the spiral. By this means the air contained in the hydrogen is deposited on the windings of the spiral. The purified hydrogen escapes through the paper cylinder d, the copper tubes d_2 and d_3, and the regenerator d_4.

The liquid hydrogen is supplied through a_1, and the insulated tube a_1, a_2, to the lower end of the vaporising spiral a_3. To ascertain how much liquid hydrogen must be supplied, the temperature of the purified gas as it enters the cylinder d_1 is determined by means of a hydrogen thermometer. (A resistance thermometer e, is also used; e_1, the cylinder on which the platinum wire is wound, e_2, the leads).

The hydrogen thermometer is arranged exactly the same as the helium-filled control thermometer in the apparatus for liquefying helium (cf. Comm. N^0. 108), f_1 is the german-silver reservoir, $f_2\, f_3$ the steel capillary, f_4 the stem, f_5 the manometer reservoir. The pressure of the hydrogen at 0° C. is chosen so that at the boiling point of hydrogen, the mercury reaches a mark at the upper end of the stem. (The pressure is then 7 cm.). The sinking of the mercury in the thermometer stem gives warning when there is not sufficient liquid hydrogen in the spiral; the supply of liquid hydrogen is so arranged that the mercury oscillates between two fixed marks.

The german-silver cap, g, is attached to the vacuum vessel by means of a rubber sleeve, and projects so far over the vacuum glass that the rubber does not become cold. The upper portion of the cap, g, and the regenerator are protected from external sources of heat by capoc.

As a rule, the velocity with which the hydrogen to be purified is supplied is so regulated that 5 M^3. per hour flow through the apparatus. In that case 4 litres of liquid hydrogen per hour are needed. This rate of production, however, cannot be kept up continuously on account of the fall of pressure in the cylinders containing the hydrogen to be purified, and of various preparatory and auxiliary operations, such as analyses, the coupling and changing of vessels with liquid hydrogen, etc. The time necessary for the manufacture of the liquid hydrogen and for compressing the purified hydrogen into cylinders must also be taken into account. The purification of 10 M^3. as a general rule is the work of one day i.e. 8 working hours. On such a working day 25 litres of liquid air are used.

Of course, the purer the hydrogen supplied to it the longer can the apparatus remain in action Hence, if commercial hydrogen [1]) is to be purified, the liquid air separator of Comm. N^0. 94 sect. XI is coupled to the apparatus here described. If that be done, the apparatus can be worked for hours without stopping. The gas which issues from the apparatus is practically perfectly pure.

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[1]) The percentage impurity changes very irregularly, being sometimes quite small and sometimes very considerable in amount.

It has now become an easy matter to obtain pure hydrogen suitable for liquefaction in the hydrogen cycle, if the precaution is taken that a certain minimum store (in Leiden 10 M^3.) of pure hydrogen is always available, which with the present apparatus is now a matter of no difficulty. Formerly, when quite pure hydrogen was a costly commodity, many experiments were obstructed by the precautions necessary to properly collect the hydrogen that had evaporated; but now one need no longer be afraid of sacrificing pure hydrogen, if necessary, and since this is the case, the great objection to its being sent away is removed.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 109c.

* * *

J. P. DALTON, M.A., B.Sc., CARNEGIE Research Fellow. "Researches on the JOULE-KELVIN effect, especially at low temperatures. II. The JOULE-KELVIN effect for air at 0°C. and at pressures up to 42 atmospheres." (*With two plates.*)

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam*, 23 April 1909, pp. 1057—1067).

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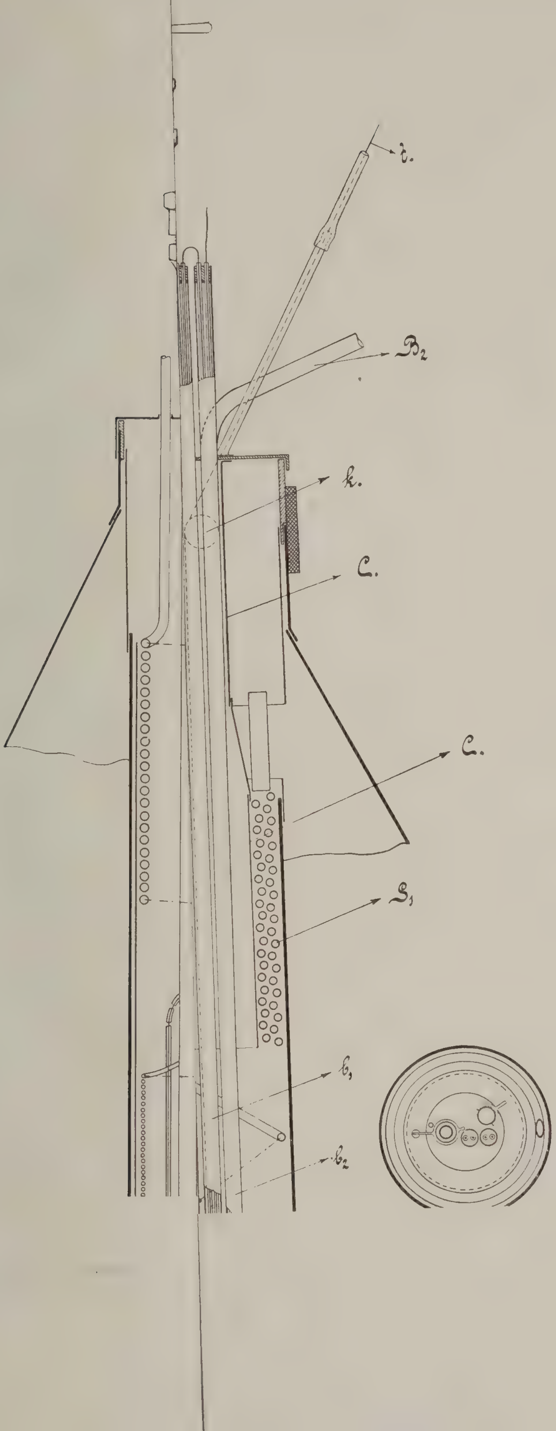
J. P. DALTON
Joule-Ke



J. P. DALTON. "Researches on the Joule-Kelvin effect, especially at low temperatures. II. The Joule-Kelvin effect for air at 0° C and at pressures up to 42 atmospheres".

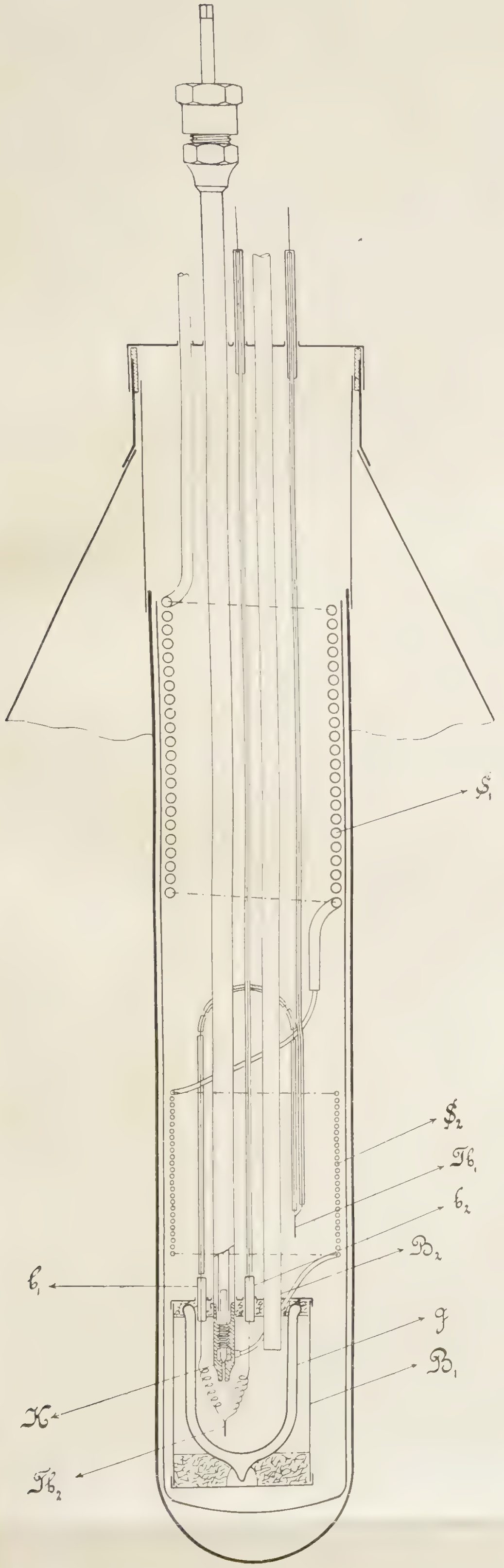


Fig. 1.

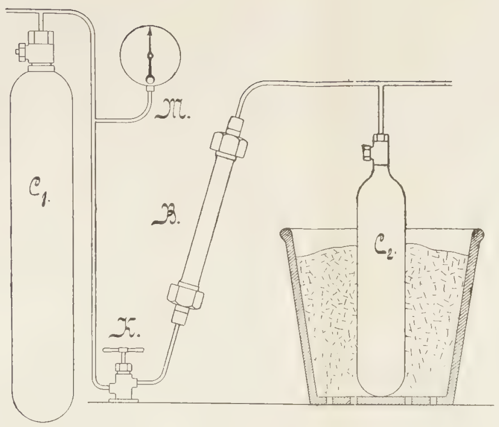


Fig. 2.

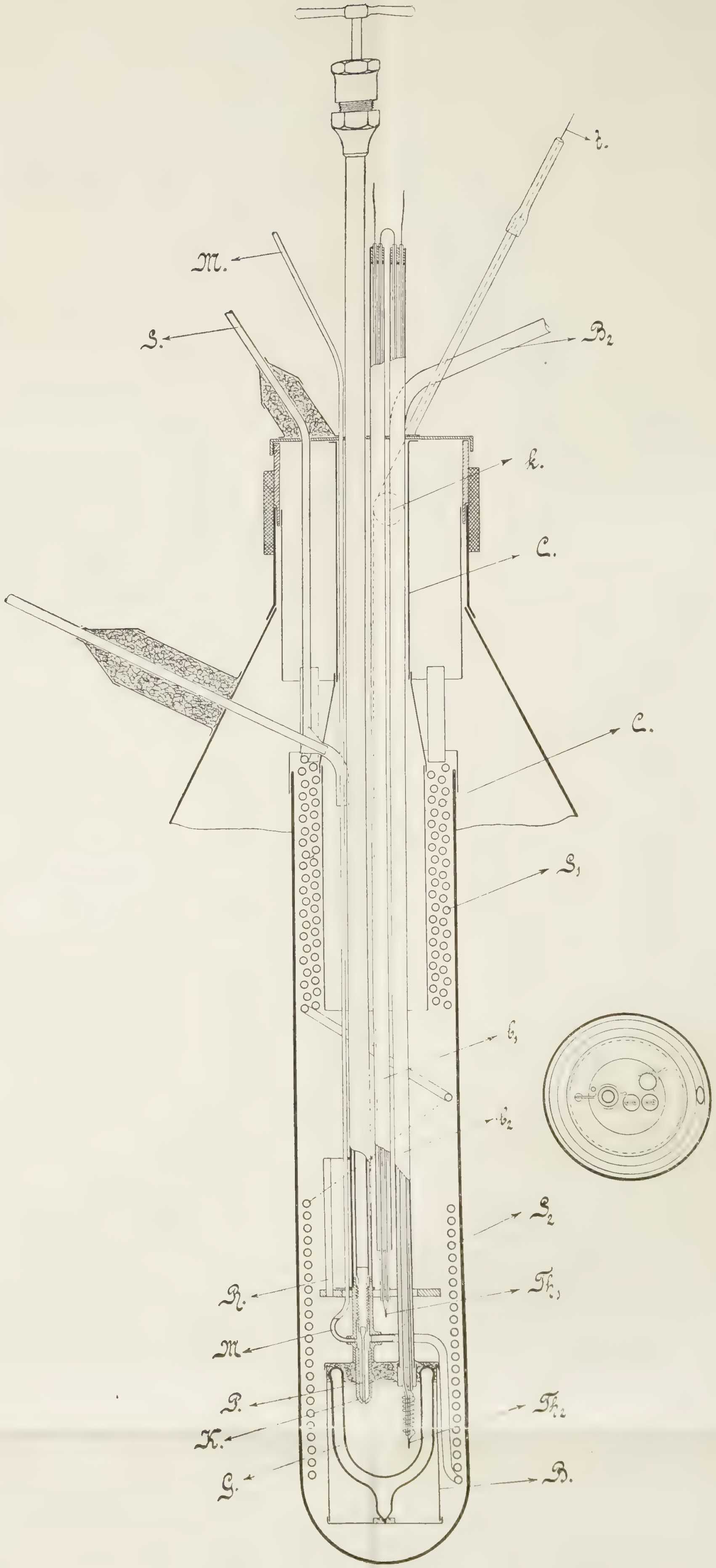
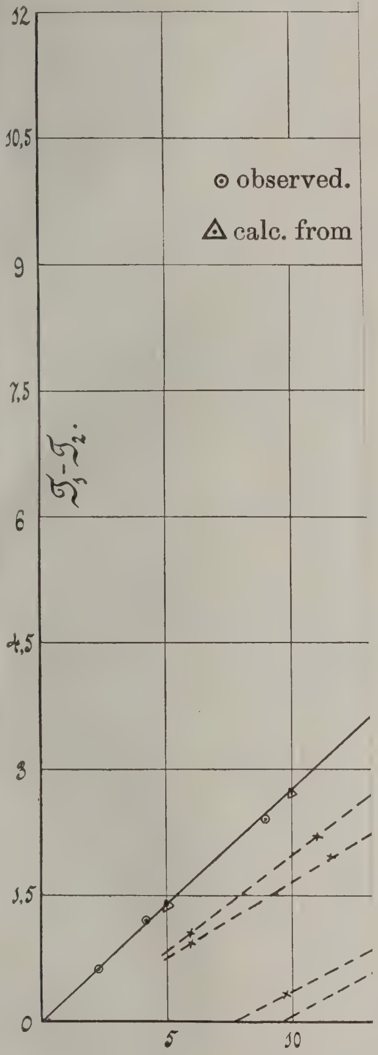


Fig. 3.

Communication No. 109c.

J. P. DALTON. "Researches
Joule-Kelvin effect for



Communication No. 10

J. P. DALTON. “Researches on the Joule-Kelvin effect, especially at low temperatures. II. The Joule-Kelvin effect for air at 0° C and at pressures up to 42 atmospheres”.

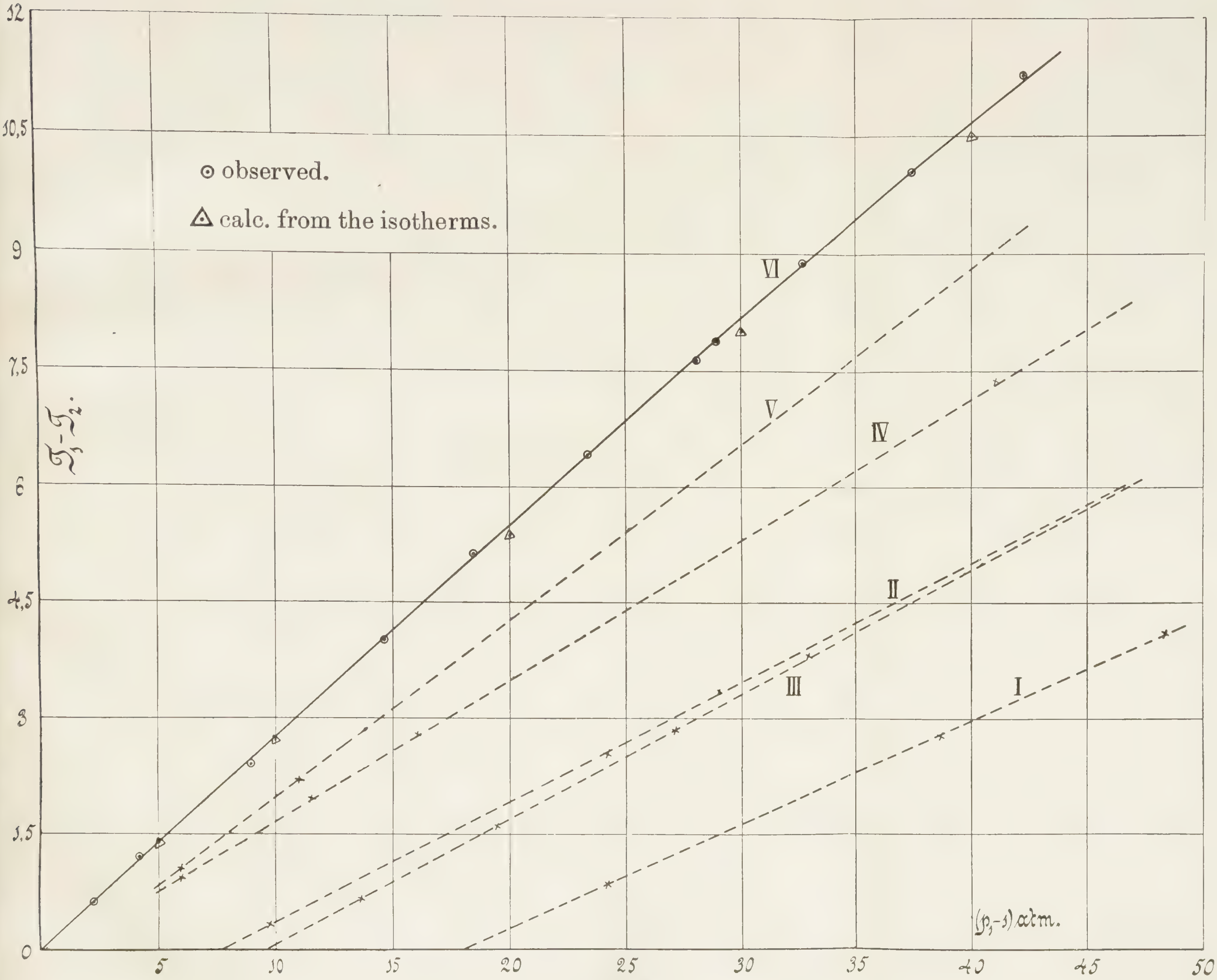


Fig 4.

Communication No. 109c.

J. P. DALTON, M.A., B.Sc., Carnegie Research Fellow. "*Researches on the* Joule-Kelvin *effect, especially at low temperatures.* II. *The* Joule-Kelvin *effect for air at 0°C. and at pressures up to* 42 *atmospheres.*"

§ 1. In a former communication (Comm. No. 109*a*) the conclusion was reached that the conditions under which Olszewski's expansions took place were not those whose fulfilment is necessary for the realisation of a true Joule-Kelvin process. The present communication offers further justification for that conclusion; it shows that special precautions are necessary before a reduction-valve apparatus, such as Olszewski used, will give a true Joule-Kelvin effect, and deals with the experiments leading to, and with the construction of, a reduction-valve apparatus particularly adapted to a determination of Joule-Kelvin effects at low temperatures. The results obtained with this apparatus in the case of air at 0°C. are in good agreement with those calculated from the isotherms, and also with those experimentally determined by Joule and Kelvin.

§ 2. The calculation from the isotherms was made in the same manner as that for hydrogen (see § 6 Comm. 109*a*). Three terms of the empirical equation of state seemed sufficient for the present purpose. It may, therefore, be written

$$pv = A + \frac{B}{v} + \frac{C}{v^2} \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and leads to the relation

$$\overline{C}_p \, (T_1 - T_2) = \frac{T\frac{dB}{dT} - 2B}{A} (p_1 - p_2) +$$

$$+ \frac{1}{2}\left[\frac{A\left(T\frac{dC}{dT} - 3\,C\right) - 2\,B\left(T\frac{dB}{dT} - 2\,B\right)}{A^3}\right](p_1^2 - p_2^2) \; . \; . \quad (3)$$

The values of the virial-coefficients for air were kindly placed at my disposal by Professor KAMERLINGH ONNES; at present they are known only for individual isotherms, and, therefore, the evaluation of their rate of change with temperature cannot be made with the same degree of accuracy as was the case with hydrogen; it is, however, sufficiently accurate for the purpose of checking the experimental results. The data employed in the calculation are

$$A_{A0^\circ} = 1.0006$$

T	$B_A \times 10^3$	$C_A \times 10^6$
0°C.	-0.57440	$+2.9594$
20°C.	-0.40495	$+3.0178$
99.4°C.	$+0.25075$	$+3.5669$

If the value of $\overline{C}_p = 0.2389$ cal. is used, and if expansion always takes place against atmospheric pressure, equation (3) gives for the cooling effect in air at a temperature of 0°C. the relation

$$T_1 - T_2 = 0.273\,(p_1 - 1) - 0.000208\,(p_1^2 - 1).$$

This is in good agreement with the JOULE-KELVIN experiments which were carried out with pressures up to 6 atm. and satisfied the relation

$$T_1 - T_2 = 0.275\,(p_1 - p_2)\left(\frac{273}{T}\right)^2.$$

§ 3. A diagram of the first apparatus used is shown in fig. 1, and it can be seen that it did not differ much from that described by OLSZEWSKI [1]). Two spirals of copper tubing, s_1 and s_2, joined in series served to bring the gas to the required temperature; s_1, in front of which was coupled a manometer, was 5 m. long and of 3.5 mm. bore; s_2, 7 m. long and of 1.25 mm. bore [2]), ended in a reduction valve K, which opened into a small silvered vacuum-vessel, g. This vacuum glass was enclosed in a german-silver box, B_1, having free communication with the outside through a wide tube, B_2, and was protected from radiation from above by felt faced with nickel-paper. Instead of a resistance thermometer as used by OLSZEWSKI, a thermoelement served to indicate the difference in temperature between the compressed and expanded gas. One junction, Th_1, was in the liquid bath surrounding the spirals, and the second, Th_2, the wires of which were insulated by short glass tubes, b_1 and b_2, soldered into the top of the box, was in the expansion chamber, g. By this means a direct measurement of the heat-effect was possible.

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[1]) K. OLSZEWSKI. Phil. Mag. [6]. 3. p 535 (1902).
Ann. phys. 7. p. 818. (1902).

[2]) This cross-section was taken so small on account of the low temperature of the liquid hydrogen in which the apparatus filled with helium was to be placed, and because at that time pure helium was still very difficult to obtain.

§ 4. The thermoelement was Platinum-Constantin, the wires of which had been carefully annealed [1]). The Platinum-Copper junctions were "protected" by copper caps, according to the method generally adopted in this laboratory (Comm. No. 27). The electromotive forces were measured by compensation against a battery of five standard WESTON-cells in parallel by means of the potentiometer arrangement already published (Comm. No. 89). The thermoelement was calibrated in steam, oil bath at ordinary temperature, liquid nitrous oxide, liquid air, and liquid hydrogen; in N_2O and liquid air by comparison with a gold resistance thermometer, and in liquid hydrogen by comparison with a platinum resistance thermometer. Both these resistance thermometers had been previously calibrated with the standard hydrogen thermometer (Comms. Nos. 95*c* and 99*c*). The sensitivity of this thermoelement is greatly diminished in the neighbourhood of liquid hydrogen temperatures; but at higher temperatures it proved sufficient for the present purpose.

§ 5. Fig. 2 shows the arrangement of the apparatus used for producing the gas-stream and maintaining it at constant pressure. A BROTHERHOOD-compressor, capable of compressing 10,000 litres per hour kept the cylinder C_1 (capacity 25 l.) filled with dry air at a pressure of 70—80 atm., the pressure being indicated by a manometer M. The pressure in the expansion apparatus was regulated by means of the valve K, and its value was indicated by a second manometer attached immediately in front of the first copper spiral [1]. To intercept any moisture that might have found its way inside the connections, a drying-tube, B, filled with solid KOH was inserted after the valve K. A small pressure cylinder, C_2, of 2—3 litres capacity, surrounded with ice, proved of considerable advantage in keeping the expansion pressure constant and in minimising the disturbing influence of possible irregularities in the flow of gas. After C_2 was coupled the expansion apparatus of fig. 1 with a manometer. The cooling spirals were immersed in water contained in a glass vessel, and this was completely surrounded by ice in a large earthenware pot. Before making a series of experiments, the apparatus was allowed to stand in ice for 3—4 hours, so as to take up the same temperature throughout; the absence of current in the galvanometer showed when the temperature within the expansion chamber was the same as that of the surrounding bath.

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[1]) For experiments with helium at the temperature of liquid hydrogen, the thermocouple gold-silver would be preferable. (See Comm. N°. 107*b*).

When an expansion was commenced, the deflection caused by the thermoelectric current in a HARTMANN and BRAUN dead-beat galvanometer (Comm. No. 89) was watched; when the deflection became constant — usually in 3—5 minutes — showing that a steady state was reached, the electromotive force was measured by the potentiometer, accurate compensation being obtained by switching in an astatic DUBOIS and RUBENS protected galvanometer (cf. Comm. No. 89). When one measurement was completed, the valve K was altered until the next pressure in the series was reached, and the series of operations was repeated.

§ 6. Expansions made with this apparatus were, however, something unusual as is at once evident from

TABLE I.

Series I. Brass valve A. Air at 0°C. 12/12/07.

(p_1-1)	T_1-T_2
9.7 atm.	warming effect
19.4	do.
24.2 „	+ 0.86°C.
29.0 „	+ 1.49 „
38.7 „	+ 2.76 „
48.4 „	+ 4.10 „

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[1] It will be seen later that the pressure indicated by the manometer was not the actual pressure at which expansion took place.

The fact that a warming effect was observed at lower pressures at once led to the suspicion that heat was being conducted along the valve to the expanding gas. During expansion, the gas-jet attains a high kinetic energy, and, correspondingly, an abnormally low temperature, and this kinetic energy is re-converted into heat only when the gas comes to rest after expansion; hence the expanding gas can take up heat from the valve, which, when added to that given by the reconversion of the kinetic energy, causes the final temperature to become too high.

To determine the influence upon the heat-effect of the quantity of gas issuing from the valve, this was opened wider and another series of measurements made.

TABLE II.

Series II. Brass valve A. Air at 0°C. 12/12/07

(p_1-1)	T_1-T_2
4.8 atm.	warming.
9.7 „	+ 0.34°C.
14.5 „	+ 1.04 „
19.4 „	+ 1.72 „
24.2 „	+ 2.53 „
29.0 „	+ 3.35 „

Hence, increasing the flow of the gas gave increased cooling effects. Further experiments showed that this was so only up to a certain point; at a given pressure difference the cooling effect observed as the valve opening increased soon attained a maximum and diminished as the valve reached its maximum opening; but this was due to the fall of pressure along the spiral, to which further reference will be made in § 9.

The assumption that the irregularity observed is due to heat conduction obtains further support from these experiments, for heat conduction for a given temperature difference between the compressed and expanded gas is constant, while the quantity of cooled gas depends, for a given pressure, upon the opening of the valve.

§ 7. At first it was thought that the conduction of heat was due to the construction of the valve, which was such that the expanded jet had to pass for a short distance along the brass walls of the valve immediately after its formation (see fig. 1). A second valve *B* was then constructed so that the contact of the expanded jet with the material of which the valve was made was reduced to a minimum. Further series of measurements were made with this new valve, but there was no improvement in the results. As before, warming was observed at the lower pressures, and, on opening the valve wider, the cooling observed at any given pressure increased, reached a maximum, and then diminished. The following are the maximum values :

TABLE III.

Series V. Brass valve *B*. Air at 0°C. 18/2/08.

(p_1-1)	T_1-T_2
3.9 atm.	warming.
7.7 „	"inversion"
13.6 „	+ 0.67°C.
19.4 „	+ 1.58 „
27.1 „	+ 2.84 „
32.9 „	+ 3.80 „

From this it was evident that heat was being conducted along the metal valve during the formation of the jet, and that as long as a valve made of conducting material was employed the proper adiabatic conditions of expansion could not be fulfilled.

§ 8. It remained to repeat the experiments using a valve of non-conducting material. Preliminary attempts to construct a wooden valve failed, for the wood used was too porous to withstand a pressure of more than a few atmospheres without leakage. Glass was next tried, and gave considerable trouble, for though very carefully annealed, the glass valves frequently broke before a pressure of 20 atmospheres was reached. Glass pins ground so as to close the valves proved quite useless, for the points got constantly broken off and plugged the valve. Eventually a glass valve closed by a wooden pin was used; it was tested up to 70 atmospheres, and although not quite pressure-tight, it closed sufficiently well for the purpose. The metal valve, *K*, was removed, and the glass one soldered in its place. The glass-copper junction was made (cf. Comm. No. 27) according to the method of CAILLETET by first platinising the glass in the blowpipe, then coppering it electrolytically, and finally, soldering it in the usual way. The junction proved most effective, and successfully resisted a pressure of 70 atm.

§ 9. It is evident from the following results which were obtained with this form of apparatus, that the warming effects previously observed at low pressures have been eliminated by the use of a non-conducting valve.

TABLE IV.

Series XII. Glass valve. Air at 0° C. 30/3/08.

$(p_1—1)$	$T_1—T_2$
6 atm.	0.92^4° C.
11.5 „	1.97 „
16 „	2.78 „
21 „	3.67 „
31 „	5.47 „
41 „	7.37 „

That these results, although heat conduction has been successfully eliminated, by no means agree with the JOULE-KELVIN experiments nor with the results calculated from the isotherms in § 2, is due to the fact that the spiral s_2 was so narrow as to cause a considerable fall of pressure along the tube; and at this temperature the pressure fall is too great to allow of the correction being calculated with sufficient accuracy.

This correction became smaller when the narrow tube, s_2, was replaced by two of 2.5 mm. bore in parallel. The following results were thus obtained:

TABLE V.

Series XIV. Glass valve. Air at 0°C. 6/4/08.

$(p_1—1)$	$T_1—T_2$
6 atm.	1.054°C.
11 „	2.21 „
16 „	3.35 „
21 „	4.62 „
30 „	6.34 „

The correction, however, is still too great to allow of its being applied with sufficient accuracy.

In order to ascertain exactly at what pressure expansion was taking place, the apparatus was so altered that a manometer might be attached directly to the expansion valve at the end of the second spiral. This, of course, does not show the true hydrostatic pressure, but calculations of the speed of the gas stream before expansion showed that the difference was negligible.

In the series of expansions undertaken after this change, only one value was obtained, for, on raising the pressure, the valve, which up till now had worked admirably, gave way, and further experiments had to be abandoned. That one value, however, viz.:

Series XV. Glass valve. Air at 0° C. 8/4/08.

(p_1-1)	(T_1-T_2)
5 atm.	1.36° C.

gave a cooling effect of 0.272° C. per atmosphere pressure difference, in good agreement with the JOULE-KELVIN and calculated values.

§ 10. Advantage of the experience gained in these preliminary investigations showing the special difficulties to be guarded against was taken in the construction of a new apparatus. In fig. 3 the apparatus is shown *in situ* in the cryostat into which liquid hydrogen may be introduced. The gas whose JOULE-KELVIN effect is to be determined enters the apparatus by the tube s, which is well protected from external sources of heat; it passes through the spiral s_1, consisting of 10 m. of copper tubing of 3.5 mm. bore, doubly wound, and is there cooled by the vapour arising from the liquid gas in the cryostat: thence it passes to the spiral s_2, which is in the liquid bath at the experimental temperature; this spiral is also of 3.5 mm. bore, and is 5.3 m. long. The tube m leads to a manometer by which the expansion pressure of the gas is indicated. From the spiral s_2, the gas enters the expansion valve, K, the flow being regulated by the wooden pin, p, and, expanding into the vacuum vessel, g, it escapes through the wide tube B_2. As before, the vacuum glass, g, is enclosed in a german-silver box, B_1, and is protected from radiation from above. A thermoelement, one junction of which, Th_1, is in the liquid bath, and the other, Th_2, in the expansion chamber gives the difference between the temperature of the gas before and after expansion. The method of insulation has been altered, for the glass tubes (b_1 and b_2 in fig. 1) gave continual trouble by breaking at inopportune moments. In the new apparatus the thermoelement wires, enclosed in glass capillaries, are led down through the german-silver tubes b_1 and b_2, from the top of the apparatus. By means of a stirrer, *R*, worked by a string, *t*, passing over a pulley, *k*, the liquid bath is agitated and the temperature kept uniform. Heat conduction to the upper portion of the apparatus is minimised by enclosing it in a german-silver cylinder, *c*.

§ 11. A new series of experiments was made with air at 0° C. using this apparatus and the arrangement of fig. 2.

TABLE VI.

Series XVIII. Glass valve. Air at 0°C. 15/3/09.

(p_1-1)	T_1-T_2
2.29 atm.	0.621°C.
4.19 „	1.207 „
9.00 „	2.410 „
14.63 „	4.030 „
18.45 „	5.136 „
23.33 „	6.410 „
28.09 „	7.643 „
28.93 „	7.888 „
32.66 „	8.894 „
37.46 „	10.026 „
42.21 „	11.300 „

The results of this and the previous series of experiments are shown graphically in fig. 4, where the ordinates represent cooling effects and the abscissae observed pressure differences. Values calculated from equation (3) are also plotted, showing good agreement between observed and calculated effects.

§ 12. The question still remained if to the observed results a correction should have to be applied for possible heat conduction to the gas during expansion. Further experiments were therefore made with a view to determining the influence upon the observed cooling effect of the quantity of gas issuing from the valve. At very small valve-openings, when the quantity of gas expanding was small, the thermoelement registered a temperature that was markedly higher than that obtained with greater valve openings; but as the valve opening increased, the cooling effect rapidly became greater, and a state was soon reached when further increase in the quantity of gas passed through the apparatus had no further measurable influence upon the observed cooling effect.

For instance, with air at 0°C. expanding from a constant pressure of 5.16 atm. the following results were obtained:

Litres per minute.	Cooling °C. p. atm.
5.5	0.244
8.2	0.258
11.4	0.272
12.0	0.273
12.8	0.273
14.0	0.273

That too small a cooling effect was observed at small valve openings may be result of conduction of heat along the glass valve, and of insufficient cooling of the thermoelement (which must constantly receive some heat from outside by radiation and heat-conduction), although even with the smallest valve openings used, the air in the vacuum glass is swept out in less than a second. The fact, however, that a final condition is reached which is independent of the velocity seems to show that the correction to be applied for heat conduction decreases very rapidly with increasing velocity [1]), and does not come into account in my experiments The explanation of this circumstance can be given only after further experiments.

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[1]) At the above pressure, the valve did not allow greater velocities to be used.

§ 12. From the foregoing it is apparent that:

1°. For experimental determinations of the JOULE-KELVIN effect with a reduction valve apparatus special precautions must be taken to observe the true expansion pressure, and to ensure absence of heat conduction to the expanding jet.

2°. The special apparatus here described gives a JOULE KELVIN effect for air at 0°C. agreeing with the experimental results of JOULE and KELVIN, and with those calculated from the experimental isotherms.

It is perhaps worth noting that in the practical application of the JOULE-KELVIN effect in the LINDE-HAMPSON process for liquefying gases, in which a reduction valve which is a good conductor of heat is used, heat conduction from the valve to the expanding gas becomes of much less importance than in an accurate determination of the JOULE-KELVIN effect, for in that case the valve and the tube which conducts the gas to it are themselves cooled in the process of regeneration by the expanded gas.

In conclusion, I gratefully acknowledge my indebtedness to Prof. H. KAMERLINGH ONNES, who invited me to undertake this research and to Prof. J. P. KUENEN for their continued interest in my work and for their helpful advice, and also to the CARNEGIE Trust for a grant in aid of the expenses of the research.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

Director of the Laboratory.

No. 110.

HENRI and JEAN BECQUEREL, and **H. KAMERLINGH ONNES**. "On phosphorescence at very low temperatures." (*With two plates.*)

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HENRI and JEAN BECQUEREL, and H. KAMERLINGH ONNES. "*On phosphorescence at very low temperatures.*"

§ 1. *Introduction.* It is known that in the case of the salts of the rare earths both in their crystalline form and in solution, absorption spectra with particularly clear and fine lines can be obtained by the application of very low temperatures, and that the investigation of the optical and magneto-optical properties of these substances at the temperatures which can be reached by means of liquid air and liquid hydrogen opens up a new method for the study of selective absorption [1]).

A problem, not less important than this, is that of the emission of light at temperatures below that of beginning incandescence. For certain substances, such as the *uranylsalts* [2]), there exists such an intimate connection between the bands in the emission spectra of their phosphorescence and the bands of their absorption spectra, that their distribution in each spectrum follows the same law, so that the bands in the one spectrum form the continuation of those in the other, while they have even two bands in common. Any peculiarity in the occurrence of one of the bands in any of the compounds periodically recurs in all the other bands, as well in the emission as in the absorption spectrum.

Thus, when the absorption spectrum of any of the uranyl compounds changes when brought under the influence of a very low temperature, the same change it also to be expected in the emission spectrum of its phosphorescence. This expectation is fully supported by our experiments. The more or less broad and diffuse bands which follow each other in regular sequence in the spectra of the uranyl salts at ordinary temperature, are, at the temperature of liquid air, resolved into multiple bands, which, in some cases, are particulary fine and intense; in that respect, all the bands in both emission and absorption spectra undergo identical changes. The appearance of these spectra at liquid air temperature has already been described [1]). At the Leiden cryogenic laboratory we have extended the investigation of these phenomena to the temperature of solid hydrogen (14° K.), and the most important of the results thus obtained concerning emission spectra at very low temperatures are here published.

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[1]) JEAN BECQUEREL 1906, 1907, 1908, 1909, le Radium t. IV. p. 49. p. 107, p. 328, p. 383, t. V. p. 5; Physik. Zeitschr. t. VIII p. 632, p. 929.

JEAN BECQUEREL and H. KAMERLINGH ONNES Comm. N^0. 103. C. R. t. CXLVI p. 625. le Radium t. V p. 227.

[2]) EDMOND BECQUEREL Mém. de l'Ac. d. Sciences t. XL. Ann de Ch. et de Phys. 5e ser t. X p. 5. HENRI BECQEREL. C. R. t. CI 1885 p. 1252.

§ 2. *Experimental method.* The apparatus here used for the investigation of the spectra of phosphorescence was the same as that which had already served for the investigation of absorption spectra, and for a description of which we refer to former papers [2]).

Here we have only to mention that the source of the spectrum was a Rowland plane grating with a lens of 1.30 m. focal length arranged in auto-collimation, and that the phosphorescent substances, enclosed in thin-walled glass tubes, were placed in a non-silvered vacuum vessel containing liquid hydrogen; in the latter case the glass containing liquid hydrogen was placed in a second vacuum vessel with liquid air so as to reduce the vaporisation of the hydrogen. The light of an-arc-lamp, filtered through an ammoniacal solution of copper sulphate, served to illuminate the salts.

§ 3. *Behaviour of the spectra when the temperature is lowered. The displacement and the limiting position of the phosphorescence bands of uranyl salts.*

When uranyl salts are cooled to a temperature of 14° K. (solid hydrogen), the lustre which they show at ordinary temperature is not diminished, and still vanishes with the illumination. Hence, *lowering of the temperature of uranyl salts in no way prevents nor prolongs their emission of light.*

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[1]) Henri Becquerel C. R. t. CXLIV 1907 p. 459 en p. 671.

[2]) Comm. N°. 103. Le Radium t. V. p. 227.

The bands which, between ordinary temperature and that of liquid air already undergo subdivision, become groups of much finer lines at the temperature of liquid hydrogen.

Fig. 1 which gives a part of the spectrum of the double sulphate of potassium and uranyl at temperatures of 288° K. (ordinary temperature), 80° K. (liquid nitrogen) and 20° K. (liquid hydrogen), shows this very clearly. The group in the bluish green is very weak, but three groups of bands in the green are very strongly developed. The manner in which the broad, diffuse patches at ordinary temperature are resolved at the lower temperatures into groups of bands is here strikingly shown. Figs. 4 and 5 (obtained with the second spectrum of the grating) give the details of some groups of bands of the same salt. Some bands which still remained complex at 80° K. have been resolved between 80° and 20° K. The spectra *a* and *b* of fig. 1 were obtained alongside each other upon the same plate by projecting the image of the phosphorescent salt upon two different parts of the slit in succession. From them we can see that *by lowering the temperature the emission-maxima are displaced towards the smaller wave-lengths.* This has already been observed[1], but it was not then shown that the displacement of the maxima was the result of a change in the period of vibration; it could also have been the result of an unusual strengthening of bands which existed already at ordinary temperature but had then a very small intensity. The observation of the spectrum at temperatures at which the bands are distinctly separated from each other shows that we have here to deal with a displacement resulting from the lowering of the temperature. The following measurements, obtained by comparison with the iron spectrum, show a distinct displacement of the bands in the case of the double sulphate of uranyl and potassium between 80° K. and 20° K.

	μμ	μμ	μμ	μμ
80° K.	511.48	534.24	559.09	586.31
20° K.	511.35	534.10	558.89	586.05.

Between 80° K. and 20° K. the ratio of the displacement to the temperature difference expressed in degrees is much smaller than between ordinary temperature (288° K.) and 80° K. (It is then from 2 to $3\mu\mu$).

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[1] HENRI BECQUEREL. C. R. t. CXLIV 1907 p. 671.

The displacements obtained by further lowering of the temperature from 20° K. to 14° K. are scarcely noticeable (fig. 5 *a* and *b*), as was to be expected by extrapolation paying attention to the small difference in degrees between these temperatures. The order of magnitude is from 0.01 to 0.02 $\mu\mu$. Hence, *it is very possible that as the temperature is lowered, the bands approach asymptotically a limiting position.* Their change, therefore, is of the same nature as the change of volume and, perhaps, as the change of dielectric constant.

§ 4. *Comparison of the different groups of bands of the same salt.*

The photographs of Pl. I and II show better than any description the spectra of a number of uranyl compounds. The data for the separate spectra are given with the explanation of the figures.

The spectrum of a definite salt consists of different groups (we observed from 7 to 8), which though not quite the same, still show a very small difference between successive groups. Only the most refrangible group, some bands of which, as we shall see later, belong both to the emission and absorption spectrum, is somewhat different from the others. We shall call those bands homologous which occupy the same relative position in the different groups. Such, for instance, are the bands whose wave-lengths are marked on fig. 7 (double acetate of uranyl and sodium).

The difference in the appearance of the different groups is the result of successive ascending changes in the relative intensities of the bands in these groups. This can be seen in all the figures, especially in fig. 7. The band $566^{\mu\mu}.34$ (fig. 7) is the most intense in the least refracted group visible in the figure; in the groups succeeding this one towards the side of the smaller wavelenghts, the homologous bands $540^{\mu\mu}.45$, $516^{\mu\mu}.78$, $495^{\mu\mu}.02$ become steadily weaker, and in the blue group the band which should be homologous with the foregoing seems to have disappeared.

On the other hand, the bands which occur on either side of the above mentioned homologous series, preponderate in the more refracted portion of the spectrum, but become less distinct as the greater wave-lengths are approached.

The spectra of uranyl sulphate have the same general appearance quite independently of whether it is combined with other sulphates or not (see figs. 1, 8, 9, 10). It was noticed long ago [1]) that the structure of the spectrum depends chiefly upon the acid with which the salt is formed, and is little influenced by the other base in the double salt. But this is shown much more clearly by observations at temperatures at which the bands no longer overlap.

§ 5. *Law of succession of the bands.* One of the most important problems is to ascertain the law connecting the frequencies of successive bands. Observations at ordinary temperature had already shown that the broad bands (such as those of fig. 1*a*) were at such distances apart, that the difference between the frequencies of successive bands was almost constant[2]). But as the bands at this temperature are broad, diffuse, and complex, it was not possible to determine the accuracy of the relation. In the spectra obtained at low temperatures the wave-lenghts could be measured; this was done by comparison with the iron-spectrum which was photographed upon the same plate as the phosporescence spectrum (see, for instance, figs. 6, 7, 8, 10).

A high degree of accuracy is possible in these measurements, particularly at the temperature of liquid hydrogen: in the case of double sulphate of uranyl and potassium (fig. 6) and of the double acetate of sodium and uranyl (fig. 7) the error in the position of the principal bands is not more than ± $0^{\mu\mu}.03$. The table given on pp. 8 and 9 contains the results of the measurements for the bands of certain salts, homologous bands being placed upon the same line.

The values of wave-lengths given above were measured in air, but the differences between the reciprocal wave-lengths are reduced

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[1]) Edmond Becquerel. Mém. de l' Acad. d. Sc. t XL p. 8 en 15.

[2]) Edmond Becqerel loc. cit. § 4 etc. Henri Becquerel C. R. t. CI 1885 p. 1259.

TABLE.

Double sulphate of uranyl and potassium.

Series in which the strongest bands occur, at 20° K.

λ	490.34 μμ	—	511.35 μμ	—	534.10 μμ	—	558.89 μμ	—	586.05 μμ
$\Delta \frac{1}{\lambda} \times 10^7$		837		833		830		829	

The same series at 80° K.

λ	490.42 μμ	—	511.48 μμ	—	534.24 μμ	—	559.09 μμ	—	586.31 μμ
$\Delta \frac{1}{\lambda} \times 10^7$		836		833		831		830	

Double sulphate of uranyl and sodium.

Series of strong bands at 80° K.

λ	489.15 μμ	—	510.12 μμ	—	533.00 μμ	—	557.85 μμ
$\Delta \frac{1}{\lambda} \times 10^7$		840		841		835	

Another series of strong bands at 80° K.

λ	512.54 μμ	—	535.47 μμ	—	560.46 μμ
$\Delta \frac{1}{\lambda} \times 10^7$		837		833	

Double sulphate of uranyl and ammonium.

Series of strong bands at 80° K.

λ	491.26 μμ	—	512.45 μμ	—	535.54 μμ	—	560.74 μμ	—	588.11 μμ	—	618.40 μμ
$\Delta \frac{1}{\lambda} \times 10^7$		842		841		839		829		833	

Another series of strong bands at 80° K.

λ	493.47 μμ	—	514.78 μμ	—	538.01 μμ	—	563.33 μμ	—	590.80 μμ	—	621.57 μμ
$\Delta \frac{1}{\lambda} \times 10^7$		839		839		835		825		838	

Uranylsulphate.

Series of strong bands at 80° K.

λ	491.83 μμ	—	513.39 μμ	—	536.94 μμ	—	562.68 μμ	—	591.01 μμ	—	621.95 μμ
$\Delta \frac{1}{\lambda} \times 10^7$		854		853		852		852		844	

Another series of strong bands at 80° K.

	μμ		μμ		μμ		μμ
λ	516.02	—	539.58	—	565.40	—	593.88
$\Delta\frac{1}{\lambda}\times 10^7$		843		850		848	

Uranylnitrate.

Series of the strongest bands at 80° K.

	μμ		μμ		μμ		μμ
λ	506.96	—	530.15	—	555.46	—	583.29
$\Delta\frac{1}{\lambda}\times 10^7$		862		859		858	

Double acetate of uranyl and sodium.

Six series at 80° K.

	μμ		μμ		μμ		μμ		μμ
λ	473.25	—	493.25	—	514.86	—	538.45	—	564.27
$\Delta\frac{1}{\lambda}\times 10^7$		855		852		851		850	

	μμ		μμ		μμ		μμ
λ	495.02	—	516.78	—	540.45	—	566.34
$\Delta\frac{1}{\lambda}\times 10^7$		851		848		846	

	μμ		μμ		μμ		μμ		μμ
λ	476.23	—	496.49	—	518.49	—	542.40	—	568.58
$\Delta\frac{1}{\lambda}\times 10^7$		857		855		849		849	

	μμ		μμ		μμ		μμ		μμ
λ	476.92	—	497.21	—	519.22	—	543.16	—	569.46
$\Delta\frac{1}{\lambda}\times 10^7$		856		853		848		850	

	μμ		μμ
λ	478.58	—	499.02
$\Delta\frac{1}{\lambda}\times 10^7$		856	

	μμ		μμ		μμ		μμ
λ	479.46	—	499.92	—	522.14	—	546.35
$\Delta\frac{1}{\lambda}\times 10^7$		854		851		849	

to vacuum, so that the values given for these differences are proportional to the frequencies.

From the table it appears that *the difference between the frequencies of two successive homologous bands is practically constant, not only for the same, but also for all series of homologous bands of the same salt. Further, the values of this constant for the various salts differ but slightly from each other.*

As regards the position of the bands, the spectrum of an uranyl salt is thus represented on the scale of frequencies by successive identical groups at an equal distance from each other. The deviations from this law are, as a general rule, so small, that they can be ascribed to errors in the measurements of the wave-lengths; nevertheless there is a tendency towards decrease in the frequency-differences with increasing wave-length, and it is possible, and even probable, that there is a deviation from the law in this direction, although in that case, the deviation is extremely small.

In the foregoing we have recalled the influence of the acid upon the structure of the spectrum; now we must call attention to the fact that although these spectra are also *spectra of molecules*, which differ in the various salts, yet their character is due to the uranium, which subjects the spectra of all the salts to the law just mentioned.

The law according to which the homologous bands correspond with equal differences between the frequencies is the simplest that could connect successive lines in the spectrum.

In this connection we may recall that this law, regarded as holding with close approximation, had long ago drawn attention to the uranyl salts in particular as being, from the point of view of optical phenomena, of remarkable molecular structure. This formed the starting point of the first experiments which were undertaken with a view to discovering rays analogous to those which had been observed in vacuum tubes [1]). They led to the discovery of radioactivity.

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[1]) HENRI BECQUEREL, C. R. CXXII, p. 420. (1896).

§ 6. *Character and nature of the phosphorescence spectra of the uranyl salts.*

We have seen what the law is that governs the succession of the homologous bands in the various groups. Is, now, the disposition of the bands in the same group governed by a particular law? In the most intense portion of the green of the spectrum the bands are numerous, especially at the temperature of liquid hydrogen, forming a system in themselves. But regarding the bands at the ends of the spectrum, we find, especially in the last group in the red, that they become simpler, and in many cases there remains only a succession of bands lying close together and showing marked similarity with the groups of bands in the channeled spectra of gases (nitrogen, carbon) when these are observed with a weak dispersion. In the least refrangible groups in the spectrum of uranyl sulphate (fig. 10) this is particularly well marked. This group consists of a strongly developed head towards the side of the small wave-lengths followed by seven or eight bands at regular distances from each other, and decreasing regularly in intensity as they go further way from the head. Each of these bands is a little asymmetrical, for the side towards the smaller wave-lengths is more sharply defined than the other. The blue group in the spectrum of the same salt (fig. 11) is also a channeled spectrum, but is not so extended and seems to be formed out of various series of overlapping bands.

The bands are not sufficiently fine and especially they are not sufficiently numerous for us to examine if the successive bands in the same group and the initial bands in the various groups follow DESLANDRES' law. Nevertheless this law receives as much support as might be expected especially from the groups in the orange and red in the case of the simple sulphate.

It seems to us, therefore, that these spectra are channeled spectra of the same character as the band spectra of gases.

We have investigated if a magnetic field has any influence upon the spectra of the uranyl salts. *In a field that could exceed* 20 *Kilogauss in value, no influence even upon the narrow bands at* 14° *K. (solid hydrogen) was to be observed.*. This negative result forms a new analogy between these spectra and the band spectra of gases, which likewise, in the majority of cases undergo no change in a magnetic field, although the strength of this is raised to the highest value at present possible [1]).

§ 7. *Relation between the emission by phosphorescence and the absorption of the uranyl salts. Reversible and irreversible bands.*

In the foregoing we have recalled the existence of groups which contain at the same time emission and absorption bands. Crystals of *autunite* (double phosphate of uranyl and calcium), a mineral from which very transparent plates may be obtained by cleavage, are especially suitable for the study of absorption.

Fig. 12 shows the emission and absorption spectra in the blue and green region of the spectrum of a plate of autunite at a temperature of 14° K. (solid hydrogen). It can be seen that two bands lying very close beside each other are common to both spectra; α is well developed both as an emission and absorption band, β is strong as an emission and weak as an absorption band.

Fig. 13 gives the spectrum of autunite at 80° K.

It can be shown experimentally in a striking manner that some bands can arbitrarily become emission or absorption bands. For this purpose an intense beam of light is transmitted through the crystal plate and the position of the absorption band fixed; the intensity of the transmitted light is then diminished and at the same time the plate is illuminated by violet light whose intensity always increases. *The dark band is seen to be transformed into a light band occupying exactly the same position.* This experiment, which becomes possible at the lowest temperatures, resembles the classical experiment of the reversal of the lines in the case of the sodium-flame.

The bands in the less refrangible groups cannot be reversed; they all belong to the emission spectrum.

The marked difference between the groups which are common to both spectra, and those which belong only to the emission spectrum, can be attributed to the reversible bands whose relative intensity, compared with that of the other emission bands, is much modified by this property.

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[1]) This, however, is not generally the case. As is known, A. DUFOUR has found numerous bands in the spectra of the chlorides and fluorides of the alkaline earths which show a ZEEMAN effect, and one of us has also observed this effect in the yttrium-bands.

The experiment concerning the reversal of certain bands of the uranyl salts is the first proof that certain emission bands occupy *exactly* the same position as the absorption bands. Further, the irreversible homologous bands of the other groups correspond with vibration-frequencies of the absorbed light separated from these bands by constant differences.

There seems, therefore, to exist an immediate and simple relation between absorption and emission in the uranyl salts.

We may recall that the uranosalts, *which do not phosphoresce*, have absorption spectra in which the bands with marked regularity follow the law of succession of the emission bands of the phosphorescent uranyl compounds [1]).

§ 8. *Phosphorescence of the sulphur compounds at low temperatures.*

We have made but very few observations of the phosphorescence at low temperatures of phosphorescent substances other than the uranyl salts. As regards sulphur compounds of the alcaline earths we could add nothing to the masterly research of LENARD and KLATT[2]).

Zinc sulphide is very luminous when excited by violet light at 80° K. and remains luminous for a long time afterwards; 4 or 5 seconds after excitation ceases, the stronger radiation comes to an end, and then for a long time afterwards the zinc sulphide shines with a soft glow. From the moment that warming begins as it returns to ordinary temperature, zinc sulphide shows a particularly strong lustre.

At hydrogen temperatures the light emitted during excitation, and by warming after excitation, becomes less.

The colour of the light coming from zinc sulphide seems to be the same at various temperatures, and between 80° K. and ordinary temperature no change can be seen in spectrum, which was not unexpected seeing that the spectrum was continuous.

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[1]) HENRI BECQUEREL C. R. t. CI. 1885, p. 1252.

[2]) P. LENARD and V. KLATT, Ann. d. Phys. (4) 15. 1904, p. 225—282 and 425—672.

§ 9. *Conclusion.* The uranyl salts must be regarded as a class by themselves sharply differentiated from other classes of phosphorescent substances.

From the researches of LECOCQ DE BOISBAUDRAN, LENARD and KLATT, and URBAIN on the rare earths, the sulphur compounds of the alkaline earths, and the oxides of the earth metals, it is known that these substances in the pure state do not phosphoresce; and it appears that the influence of impurity, as was first noticed by EDMOND BECQUEREL, is essential to the formation in those substances of complex molecules, LENARD's "centra", which, as distinguished from the molecules of the substances themselves, have the power of emitting light.

It is completely different with the salts of uranyl. These compounds always phosphoresce, even when quite pure, and each of them is characterised by a specifically distinct emission spectrum.

And in other respects the uranyl salts differ from those just mentioned as phosphorescent only by the influence of admixture. Even at a temperature so low as that of liquid hydrogen, the quantity of the emitted light does not alter in intensity and vanishes with the illumination. The uranyl salts do not exhibit thermoluminescence. Finally, the spectra of these salts are of remarkable structure, while an immediate relation exists between the emission and absorption spectra.

These optical phenomena at low temperatures, by which considerable light is thrown on the characteristic properties of the phosporescence of uranyl salts, thus lead to a distinction between two kinds of phosphorescence, which seem to be of different origins. On the one hand, in the case of the rare earths, the sulphur compounds of the alkaline earths, and the oxides of the earth metals, according to the beautiful theory of LENARD [1]), the electrons, which, under the photo-electric influence of the absorbed light, are ejected by the atoms of the metal and by their return to these cause phosphorescence are supplied by that metal of which a small quantity is added to the experimental substance so as to cause it to phosphoresce by the formation of "centra", of which the structure of the molecular complexes play an important part in the phosphorescence. On the other hand, following in the track of the same theory, the explanation of the phenomena exhibited by uranyl salts must be sought in the motion of the electrons contained in the uranium atom itself and in the structure of the molecules of the substance itself.

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[1]) P. LENARD, Verh. d. Naturhist. Med. Ver. Heidelberg 5 Febr. 1909.

In this case especially considering the small obstruction cold offers to the return of the electrons [1]) the question obtrudes itself if, perhaps, the whole process of phosphorescence takes place within the uranium atom, or at least within the uranyl group, and electrons, under the photo-electric influence of the absorbed light, are projected from a part of this atom to other parts of it, remain there temporarily, and, by returning to their original position of equilibrium, cause the emission of phosphorescent light. The motion of the electrons causing phosphorescence, and therefore, the position of the bands in the spectrum will, of course, undergo different modifications for the various salts by the influence (of the electric field) of the other atoms, which with the atom of uranium form a complete molecule.

EXPLANATION OF THE FIGURES.

Fig. 1. *Potassium uranyl sulphate* *a*) at 288° K., *b*) at 80° K., *c*) at 20° K.
First spectrum, Rowland grating.
The spectra *a*) and *b*) photographed beside each other on the same plate allow a direct comparison of the positions of the bands at ordinary temperature and that of liquid nitrogen.

Fig. 2. *a*) *Autunite* (Calcium uranyl phosphate).
b) *Potassium uranyl chloride.*
c) *Uranyl nitrate.*
d) *Potassium uranyl sulphate.*
Temperature 80° K. First spectrum, Rowland grating.

Fig. 3. *a*) and *c*) *Potassium uranyl chloride.*
b) and *f*) *Uranyl nitrate.*
g) *Potassium uranyl sulphate.*
d) *Autunite* (calcium uranyl phosphate).
Temperature 14° K. Second spectrum, Rowland grating. These photos give the details of the groups at the temperature of solid hydrogen.

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[1]) The emission vanishing with the illumination.

Fig. 4 and 5. *Potassium uranyl sulphate.*
a) at 14° K., *b*) at 20° K., *c*) at 80° K.
Second spectrum, Rowland grating. Details of the groups at these three temperatures.

Fig. 6. Adjacent spectra of *a*) *potassium uranyl sulphate* at 20° K. and *b*) *the iron arc.*
Second spectrum, Rowland grating. Exemple of the measurement of wave-length; short exposure so as to make an accurate measurement possible.

Fig. 7. *Sodium uranyl acetate* at 80° K.
First spectrum, Rowland grating.
Measurement of wave-lengths, and details of the groups.

Fig. 8. *a*) *Iron arc*, *b*) *Sodium uranyl sulphate*, *c*) *Ammonium uranyl sulphate.*
Temperature 80° K.
First spectrum, Rowland grating.
Measurement of wave-lengths, and details of the groups.

Fig. 9. *Uranyl sulphate* at 80° K.

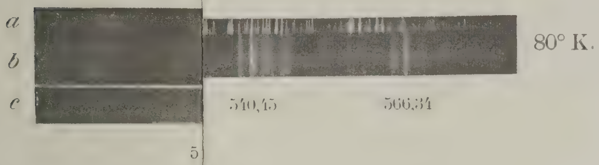
Fig. 10. *a*) *Iron arc*, *b*) *Uranyl sulphate.*
Temperature 80° K.
First spectrum, Rowland grating.
Channeled spectrum in the yellow and orange.

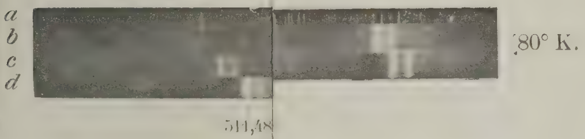
Fig. 11. *Uranyl sulphate.*
Temperature 80° K.
Second spectrum, Rowland grating.
Channeled spectrum in the green-blue.

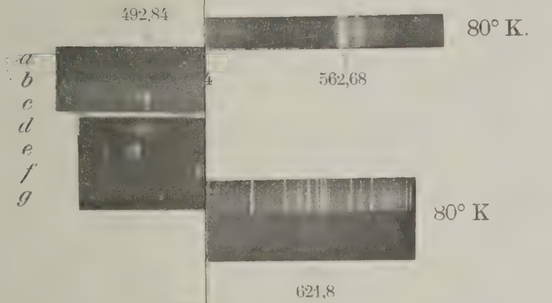
Fig. 12. *Absorption and emission of autunite* (calcium uranyl phosphate) at 14° K.
Second spectrum, Rowland grating.
a) emission spectrum, *b*) absorption spectrum, α and β, bands common to both spectra (reversible bands).

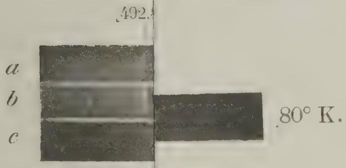
Fig. 13. *Absorption and emission of autunite* at 80° K.
First spectrum, Rowland grating.
a) and *b*) two of the chief absorption spectra of the crystal plate, *c*) phosphorescence spectrum, α) reversible band.

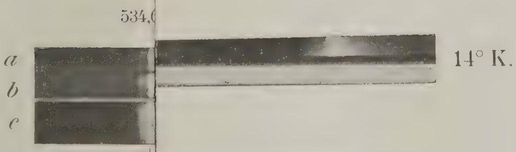
HENRI and JEAN H. KAMERLINGH ONNES.
“On phosphores temperatures.” Pl. II.

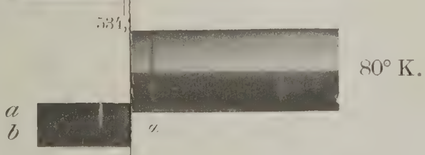












Communication N

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HENRI and JEAN BECQUEREL, and H. KAMERLINGH ONNES.
"On phosphorescence at very low temperatures." **Pl. I.**

Fig. 1.

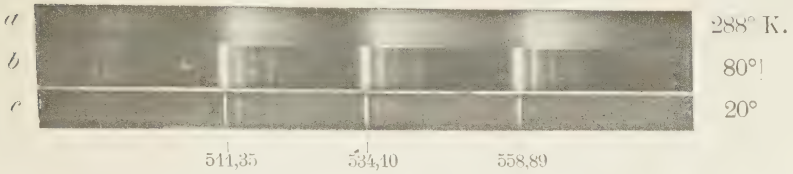


Fig. 2.

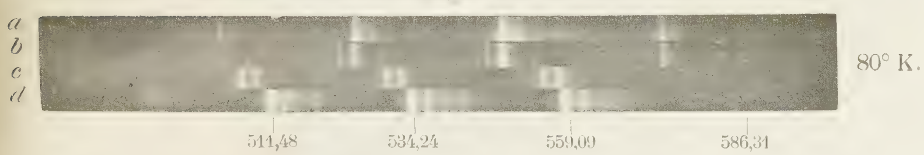
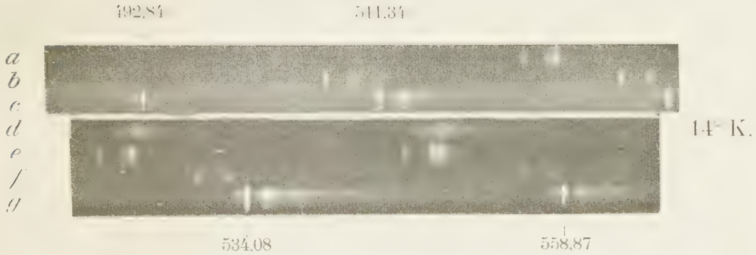


Fig. 3.



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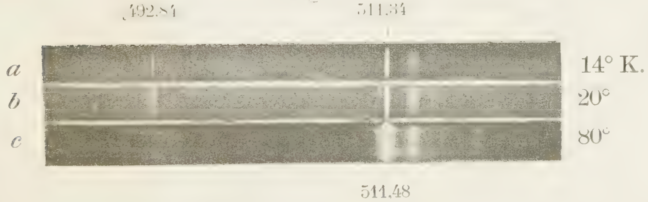


Fig. 5.

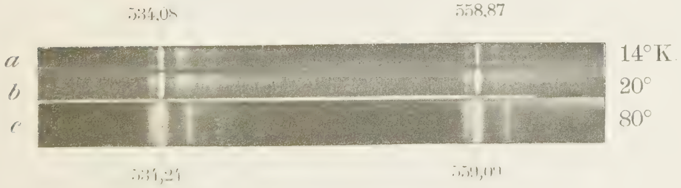
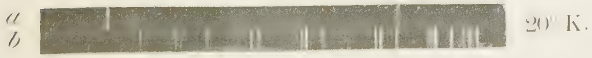


Fig. 6.



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HENRI and JEAN BECQUEREL, and H. KAMERLINGH ONNES.
"On phosphorescence at very low temperatures." **Pl. II.**

Fig. 7.

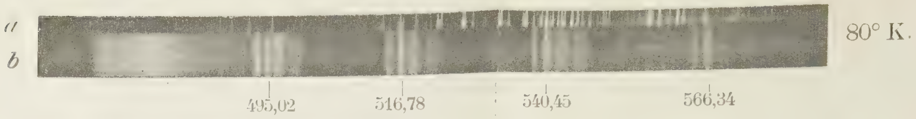


Fig. 8.

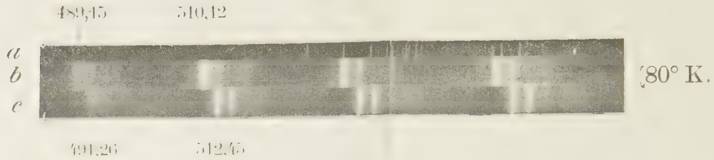


Fig. 9.

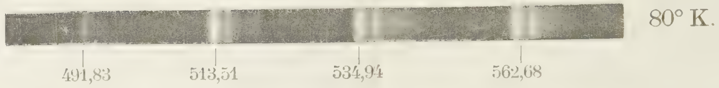


Fig. 10.

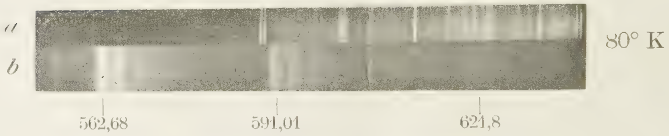
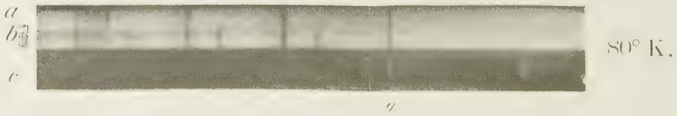


Fig. 11

Fig. 12.

Fig. 13



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Director of the Laboratory.

No. 111.

P. LENARD, **H. KAMERLINGH ONNES**, and **W. E. PAULI**. "The behaviour of the phosphorescent sulphides of the alkaline earths at various temperatures, and particularly at very low temperatures." (*With a plate.*)

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon Akademie van Wetenschappen te Amsterdam*, **26 Juni 1909**, pp. 151—168).

Eduard IJdo — Printer — Leiden.

P. LENARD, H. KAMERLINGH ONNES and W. E. PAULI.

"The behaviour of the phosphorescent sulphides of the alkaline earths at various temperatures, and particularly at very low temperatures."

Fig. 1.

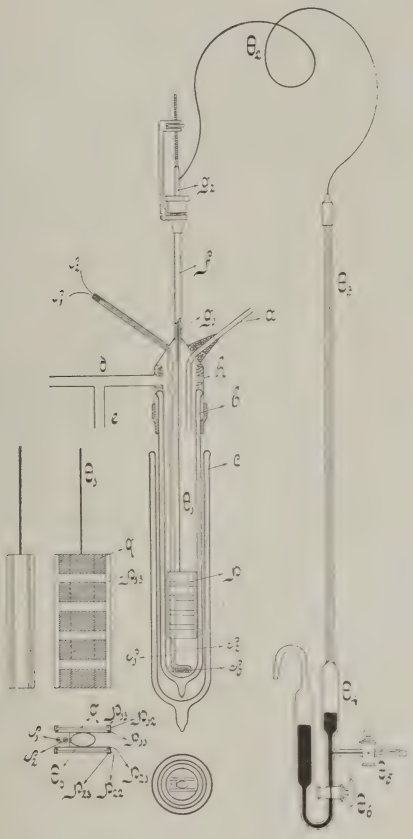
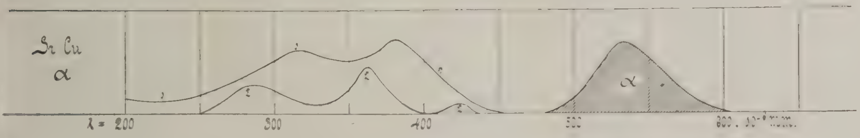


Fig. 2.



Excitation-distribution.

Band.

1. Excited intensity during illumination (momentary permanent excitation).
2. Excited intensity in the afterglow (permanent excitation).

Communication N° 111

P. LENARD, H. KAMERLINGH ONNES and **W. E. PAULI.** "*The behaviour of the phosphorescent sulfides of the alkaline earths at various temperatures, and particularly at very low temperatures.*"

§ 1. For two reasons it seemed to us of importance that the behaviour of the "phosphors" [1] of the alkaline earths should be investigated at the lowest possible temperatures. In the first place, former experiments of LENARD and KLATT [2] in which the temperature was lowered to —180° C., had already shown that the development of many emission bands in these "phosphors" would end only when the temperature was lowered still further, and it was an open question if that further development should correspond with the views already deduced ("1904", pp. 666 *et seq.*) concerning the change with temperature in the properties of the phosphorescence bands. Temperatures so low as those which may be reached with liquid hydrogen seemed to offer particular facilities for clearing up this point, for in other phenomena peculiarities which can be attributed to the fixing of electrons become prominent just at these temperatures [3].

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[1] For the sake of brevity we shall in this paper refer to a phosphorescent substance as a "phosphor".

[2] P. LENARD and V. KLATT: Ann. d. Phys. 15, pp. 451 *et seq.* (1904).

This paper which contains very numerous experimental data, and which has already indicated the main points of the theory here given concerning the processes involved in phosphorescence, shall in the sequel, for the sake of brevity, be referred to as "1904".

[3] The changes in the increase of electrical conductivity of metals with lowering of temperature noticeable at very low temperatures, in correspondence with the idea first expressed by KELVIN, that the conductivity attains a maximum value at very low temperatures (cf. KAMERLINGH ONNES and CLAY: Comm. N⁰. 95*c*, 95*d*, 99, 107*c*), were regarded by KAMERLINGH ONNES (Comm. Suppl. N⁰. 9 p. 27), following the views of P. LENARD, as a consequence of certain places (dynamids) in the atoms having the power at very low temperatures of holding electrons which, at higher temperatures, are in free motion. The different conditions of motion of the electrons between and around the dynamids were visualised as

In the second place, the suppositions concerning the mechanism of phosphorescence which were developed in "1904" could be put to the proof and extended, if we succeeded in observing any influence of the magnetic field upon the phosphorescence bands. That such an influence cannot be detected at ordinary temperature has been known for years by P. LENARD, who for this purpose investigated Ca Bi-, Ca Mn-, and Ca Ni-"phosphors" in strong magnetic fields. And as all bands at ordinary temperature are very broad and ill-defined there seemed to be no chance of making further discoveries in this direction. Now, however, it had appeared from the above mentioned experiments in liquid air, that all phosphorescence bands become remarkably narrower and sharper as the temperature is lowered ("1904" p. 455), and it seemed to be worth while examining if perhaps, at the temperature of liquid—or otherwise of solid — hydrogen the narrowing of the bands should continue so far, that a further investigation in the magnetic field would afford a new outlook upon the problem.

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three states of aggregation and it was remarked that the magnetic field should exert a similar influence as that exerted by temperature upon the transition of the electrons from one state to another.

This image was further developed in later researches by J. BECQUEREL and H. KAMERLINGH ONNES (Comm. N⁰. 103, particularly pp. 6, 9, 14) on the absorption-spectra of compounds of the rare earths and their behaviour in a magnetic field, which were undertaken also on account of the particular influence of liquid hydrogen temperatures upon the effect of forces exerted by ponderable matter upon the electrons. As "gas or vapour" state can be distinguished that state of motion in which the electrons can occasion conduction of electricity through the atoms when these are in metallic connection, by "liquid", a state of motion in which they are sensitive to light-vibrations and absorption phenomena, while, on the other hand, a "solid" state is a state of motion in which they can take part neither in conduction, nor in absorption of light.

Interpreting the results of the experiments just mentioned in terms of this theory we find that by the circumstance that at very low temperatures the sphere of influence of the dynamids extends to a greater distance the free path in the electron vapour is greatly diminished, and that hydrogen temperatures are already sufficiently low to cause the electrons at various parts of the atom to assume the solid state; these are just the places where the electrons at temperatures that are not so low are particularly numerous in the liquid state, as can be seen from the occurrence of various absorption bands.

Indeed, the researches of H. and J. BECQUEREL and H. KAMERLINGH ONNES upon the phosphorescent uranyl salts, completed last year and published [1]) after the present investigation had been commenced, were successful in this respect.

We have therefore investigated a series of well-defined "phosphors" of the alkaline earths as described in "1904" in liquid and solid hydrogen, — hence to a temperature of 14° K. The general result we first communicate here: The bands behaved quite as we expected in becoming narrower and sharper, so that the wave-lengths of their maxima could be determined at these low temperatures under very favourable circumstances. But they remained bands whose intensity did not support a strong dispersion, and this is the reason that we have for the present postponed the continuation of the experiments in the magnetic field. Our aim has rather been to study the particular temperature properties of a number of definite bands, and from these we have attempted to draw general conclusions concerning the process of phosphorescence. In this we have found the ideas already developed fully supported; in certain respects, however, some not unimportant extensions of these conceptions have been obtained and hence we publish our results here in full.

§ 2. *Apparatus*. The apparatus shown in fig. 1 was used for the experiments with liquid hydrogen. The liquid hydrogen is introduced [2]) through the german-silver tube a to the transparent vacuum glass b, which is inserted in a vacuum glass c containing liquid air. The gaseous hydrogen is led away through d to the gasometer or the vacuum-pump; e is a safety tube, and at the same time a manometer. The german-silver tube f attached to the german-silver covering by means of a packing tube allows a vertical or a rotational motion to be communicated to the rod $g_1\, g_2$.

By means of θ_1, a steel capillary which enters the opening of the hollow rod and is there soldered, the rod $g_1\, g_2$ carries two copper plates p_{11} and p_{21} which are provided with small frames

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[1]) H. and J. BECQUEREL and H. KAMERLINGH ONNES: Comm. Phys. Lab. Leiden. N^0. 110.

[2]) Cf. Comm. N^0. 103, Pl. I, fig. 4; Comm. N^0. 94f, Pl. III.

p_{12} p_{13} on the longer sides. In the copper frames p_{12} thin glass plates q can be fitted, and on these the powdered "phosphors" are scattered in a layer of varnish [1]) and fastened under a very low pressure. The front of the frame is provided with numerous incisions so that the glass plates can be clamped by bending down the little teeth formed in the process of cutting, without exposing the "phosphors" to pressure. The two plates p_1, p_2 and the screw and nut at the upper end of the smooth rod g enable one to observe different "phosphors" under the same conditions and immediately after each other.

Between the two plates p_1, p_2 lies the reservoir θ_0 of the helium thermometer which indicates the temperature of the "phosphors"; it is an elliptical cylinder of german-silver. It is attached to the steel capillary θ_1 which, enclosed in g_1, passes through the tube f, and by this means is connected with the glass capillary θ_3 which allows readings for accurate determinations of temperature between —260° C. and —180° C. and with the reservoir θ_4, on which temperatures higher than —180° C. can be read by approximation. The purpose served by the valves θ_5 and θ_6 needs no further explanation.

To the bottom of the hydrogen glass b is brought a german-silver warming coil s_0, whose leads are insulated and made air-tight in the cap h. This coil serves to vaporise the hydrogen; when this has vaporised the temperature of the space b slowly rises, and by this means the simultaneous change of the phosphorescence and of the temperature can be followed.

In order to work at the temperature of solid hydrogen, the hydrogen gas is pumped away by the vacuum-pump along d, and the pressure is lowered until a crystal layer is formed on the liquid hydrogen; after the crystal layer has grown to a certain thickness it is kept in that state by regulating the rate at which the gas is pumped away.

As the source of light for exciting phosphorescence an iron-arc was used with or without the WOOD ultra-violet filter (arranged

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1) We satisfied ourselves that the varnish used did not phosphoresce even at —260° C. At temperatures that were not so very low we had thought of using lanoline for attaching the "phosphors", but it seemed to give rise to an afterglow which in one of our substances almost led us upon a false track.

as in „1904” p. 244) which had been very suitable in former experiments, and also a carbon arc with the same filter and concentrating lenses. Ultra-red light which often proved serviceable was obtained from the same arc lamp by using as light filter a layer of water and a layer of a solution of iodine in carbon bisulphide. We found no noticeable absorption of this light in the layers of liquid air and liquid hydrogen which it had to traverse. In order to put this to the proof we so manipulated the height of the surface of the liquid hydrogen that the rays falling upon the "phosphor" passed only through glass and gas, and the "phosphor" came just above the surface of the liquid and no more, so that although in the vapour space, it remained just as strongly cooled; in these circumstances we observed not the slightest change.

The substances embraced by our experiments were the "phosphors": Ca Cu Li, Ca Mn Na (yellowshade), Ca Ni Fl, Ca Bi Na, Sr Zn Fl, Sr Mn Na, Sr Bi Na, Ba Cu Li, Ba Bi Na. They were all prepared so that they showed those bands, which will be discussed in the sequel, well developed. Phosphorescent zincsulphide, uranyl fluoride fluorammonium, and a crystal of uranyl nitrate were also examined.

§ 3. *Temperature phases.* An ample and comprehensive treatment of the change of light emission of the "phosphors" with temperature has already been given [1]).

According to that exposition of the subject, to each band of the phosphorescent light there belong three phases, which as the temperature falls succeed each other in the following order: 1^0. the upper momentary phase, or heat phase, 2^0. the permanent phase, 3^0. the lower momentary phase or cold phase. For each of the various phosphorescence bands the range of temperature embraced by the permanent phase, which also determines the two other phases, lies at a definite height upon the scale of temperatures. In the lower momentary phase the electrons which under the photoelectric influence of the illumination are ejected from the metallic atom are fixed and stored [1]) in the neighbourhood [2]); in the upper momentary phase this fixing of the electrons does not occur for they return immediately causing emission of light; in the intervening permanent phase some of the electrons return and others are fixed in the neighbourhood. It is this permanent phase in which the "phosphor" shows the long and bright afterglow of its respective band. In the earlier experiments which reached a temperature of only —180° C. the existence of the three phases remained hypothetical for a number of bands, but we are now in a position to show that for these bands the apparently missing regions of permanency and of the lower momentary phase can really be attained by a further lowering of the temperature. Thus while up to the present we observed only the momentary bands Ca Mn β, Sr Mn β, Ba Cu β_3, we have now observed the permanent phase and the lower momentary phase, and in Ca Ni β, Ca Bi γ and Ca Bi α_2, Sr Zn α, Ba Bi α_2 the hitherto unobserved lower momentary phase. Thus the prophecy formerly made („1904", p. 483, note 2) concerning these "phosphors" has now been found to be fulfilled [3]).

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[1]) "1904"; also P. Lenard: Verh. des Naturh. Med. Ver. Heidelberg, 5 Febr. 1909, pp 9, 10 *et seq.* We shall in the sequel refer to this comprehensive paper as „1909”.

As a general rule one can say about the temperature phases at very low temperatures, that *the temperature of solid hydrogen* (in round numbers —260° C.) *is low enough to bring all bands*

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[1]) All the ejected electrons are not thus stored: some of them return at once and in this way cause the momentary light during the illumination; see in this connection § 7 of this communication. This "momentary process" happens with more or less intensity (according to the exciting wave-length) alongside "the continuous process" of storing the electrons. It was in a former paper ("1904". p. 667) considered as an extreme possible case that finally in the lower momentary phase the momentary process should take place alone without any storing of electrons. In no single band, however, has this been since realised, and therefore on the contrary the storing of electrons is chosen in "1909" as the characteristic of the lower momentary phase.

[2]) By this expression we always mean parts of *the centrum itself*; it has already been shown in "1904" (p. 671) that the material which surrounds the centra has nothing to do with the retaining of the charge; cf. also "1909", pp. 14, *et seq.*, and § 7 of this communication.

[3]) The permanent yellow-red band of the Sr Mn-"phospors" which had formerly remained unnoticed on account of the smallness of the range of the permanent phase was now found to be at —60°C.

of the "phosphors" of the alkaline earths [1]) *into the lower momentary phase.* As the temperature falls from higher values to that of liquid air (—180° C.) new bands continually appear in the permanent phase. Also at the temperature of liquid air various bands are of long duration, the most striking being the persistent and clear afterglow of the Ca Ni-"phosphors" (Ca Ni β band) ("1904", p. 435). At all lower temperatures, however, down to —260° C. one can observe but a small continuous afterglow; only the orange-yellow afterglow of the Ba Cu-"phosphors" is here conspicuous for its persistence and clearness, having a maximum at —190° C. All other bands either appear in the lower momentary phase in so far as they have not already gone beyond it, or they pass through a region of permamency lying very low and of small intensity (such as Ba Cu β at —240° C., Ca Mn β at —250° C.). At the still lower temperature of —260° C. all phosphorescence becomes exclusively momentary [2]).

In all the "phosphors" investigated exposure to cold has resulted in discovery of only one new band; it is a green band in Ca Bi lying not far from the green heat band Ca Bi β, but contrary to this it is to be indicated as the lowest cold-band which assumes a state of a permanency at —255° C. although, as has already been remarked in general concerning these temperatures, the intensity is very small.

If we compare the "phosphors" of the alkaline earths with respect to their temperature phases with the uranyl salts investigated by H. and J. Becquerel and H. Kamerlingh Onnes, we find that in the latter case no results were observed which would oppose the theory that the emissions of the uranyl salts also undergo three temperature phases. Only, the permanent phase and, *a*

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1) In the present communication we have left out of account the "phosphors" of lead, silver, antimony and also of SrCu.

2) A thermoscope that would serve many purposes both at low temperatures and at others up to red-heat, could be made out of a number of small pieces of different "phosphors" enclosed in a glass tube devoid of air. These should be so chosen that the range of permanency of their bands at different points of the desired temperature interval should end as sharply as possible. The temperature could then be determined according to whether they glow or not with a definite colour when exposed to light.

fortiori, the lower momentary phase must then lie at temperatures much lower than the temperatures reached by those experimenters and by us. To their results we may add that uranyl fluoride fluorammonium behaves just the same as the other uranyl salts examined by them, while in the case of uranyl nitrate we have confirmed their results. The emissions of the uranyl salts have thus been observed only in the upper momentary phase, in which no storing of the electrons takes place; were one able to bring them to the lower momentary phase (below —260° C.), then, after illumination at that temperature, one should be able to observe a glow as the temperature rises, a result attempted but not attained by the above-mentioned experimenters at the lowest temperature reached at present ¹).

§ 4. *On the glowing of the "phosphors" as the substance is warmed from low temperatures.*

It was proved "1904" p. 458 that as a "phosphor" is warmed after excitation by light those bands appear in succession the temperature ranges of whose permanent phase succeed each other on the scale of temperatures. This appears to be the case also in the range of temperatures here investigated. If we carefully compare the glow occasioned when passing through various temperatures with the afterglow at various constant temperatures, we find that a "phosphor" that has been exposed to illumination responds as long as the temperature is within the limits of the range of the permanent phase of the band in question. That affords us a means that has proved of great service to us, of determining the range of the permanent phase for bands for which it had not previously been known. For this purpose the "phosphor" was illuminated at the temperature of solid hydrogen, and was then slowly warmed by means of the warming coil s shown in Fig. 1, and in the meantime it was watched until the glowing band for which the temperature range of the permanent phase was examined, lighted up. The temperature interval within whose limits this occurs is the region of permanency of

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1) According to § 7. of this Communication, in the case of the emissions of the "phosphors" of the alkaline earths it also depends upon the wave-length of the light used to excite the phosphorescence whether we obtain storing and therefore responsive glow, or not.

the band investigated. In this manner various experimental results given in this communication were obtained.

Thus the region of afterglow of the band Ba Cu α_2 extends from −260° C. to + 350° C. [1]), and is therefore unusually extensive; the region of warming-glow of this band is equally wide. An example of a narrow range on the other hand is given for the yellow band Ca Ni β from —180° C. to —100° C., and in this case the warming-glow is restricted to within the same narrow limits.

The storing of the effects of illumination is at the temperature of solid hydrogen particularly large and unusually complete. If, after illuminating the phosphorescent substance at —260° C. it is slowly warmed, it remains nevertheless quite or nearly quite dark; but when the lower limit of the permanent phase is passed, the emission of light begins almost at once with great intensity. It is just the non-appearance of the effects of the illumination in the lower momentary phase that makes it comprehensible that the storing should reach such a great value. Its value remains, however, beneath a certain limit. If the illumination in liquid hydrogen is continued longer and longer, the intensity of the warming-glow finally ceases to increase. This must be explained by the circumstance that as soon as the centra which occasion the bands have obtained their full charge they adopt other periods of oscillation (corresponding with the periods of the light which can extinguish the phosphorescence [2])) and could not thus in any case absorb any more of the exciting light

With regard to the intensity of the light during the illumination in the lower momentary phase, we found that for a definite exciting wave-length, *e. g.* the light passed through our ultraviolet filter, the various bands behaved in widely differing manners. Bands that at —260° C. are of very small intensity in the lower momentary phase are *e. g.* Ca Mn α, Sr Mn α, while others such as Ba Cu α_2, Ba Bi α_2, radiate with great clearness under the same circumstances. The latter, however, also lose their light quickly after illumination — a behaviour corresponding

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1) At temperatures above the ordinary, the intensity of both the responsiv glow and the afterglow with ultra-red excitation is indeed very small.

2) "1909". Also P. LENARD and SEM SAELAND, Ann. d. Phys. 28. p. 49 (1909).

with the known properties of the lower momentary phase — and show also the very perfect storing which we have just mentioned. Later (§ 7 of this Communication) we shall bring these different behaviours of the various bands under one general point of view, by making the fundamental assumption that the quantitative relation between the momentary process and the simultaneous continuous process in one and the same band differs according to the wave-length which gives rise to the processes.

§ 5. *Response to illumination by long waves (red and ultra-red) and subsequent extinction.* It has already been shown ("1909", p. 7 [1])) that the action of ultra-red upon the "phosphors" consists of a local molecular rise in temperature of the centra. If the temperature of the centrum rises so far that it enters the permanent phase region of temperature, then the substance begins to respond — previous excitation being understood — just as if the whole "phosphor" had been brought to the higher temperature. When the stored charge is used up, darkness follows the glow, and it is extinguished It has also been already shown that when ultra-red light is the exciting agent a different local molecular rise in temperature belongs to each band, also to those of the same "phosphor", and that each active metal has a particular distribution of extinguishing powers over the spectrum. Discussion of these characteristics in themselves will be reserved for a special communication; our main wish for the present has been to concentrate our attention upon the confirmation and extension of these views which have been developed from the results of observations obtained at very low temperatures.

Corresponding with the great charge which is kept stored at low temperatures, the response to ultra-red excitation at these temperatures is also very intense. As a general rule in this case the actual *lighting up* is far more striking than the subsequent extinction which here takes place far more slowly than at ordinary temperature. We may just now instance the extreme case of zinc sulphide, in which the lighting up which always precedes the extinction ("1909") escaped the notice of even a careful observer [2]).

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1) Also P. Lenard and Sem Saeland, l. c. p. 11 note 2.

2) A. Dahms; Ann. d. Phys. 1903.

If one allows ultra-red light to act upon zinc sulphide in liquid hydrogen, one observes a glow during many seconds. [1]). As other examples of response to ultra-red excitation in liquid hydrogen we may name: Ba Bi Na, extremely intense and remaining green with the α_2 and β band, hence like the afterglow at ordinary temperature, Ba Cu Li very clear, red, α_1 band, hence like the glow at ordinary temperature; and similarly Sr Bi Na with clear bluish-green responsive glow. To ultra-red excitation in liquid hydrogen those bands respond as a general rule the range of whose permanent phase does not lie too high. So in the case of SrMnNa the yellow-red band β_1, together with a little of the green band α. The region of the permanent phase for the band β_1 lies about —60° C., or very approximately between —100° C. and —45° C., that for the band α, between —100° C. and + 100° C. Hence the local temperature of the β_1 centra had not in any case risen far above —45° C., nor that of the α centra far above —100° C. The same can be seen even in liquid air. In a mixture of carbon dioxide and ether (about —50° C.) on the other hand the "phosphor" responds with a clear yellow light (α band) just like the afterglow at ordinary temperature, and then becomes dark; in this case therefore the local temperature of the α centra has already risen above + 100° C. From this it can be seen that the local temperature attainable with a given intensity of ultra-red excitation depends upon the temperature of the material filling the space surrounding the centra. Apparently the centra attain that temperature at which the energy communicated to them by the ultra-red excitation is equal to the energy given in the same time to the surrounding material in the form of molecular motion; an equilibrium is established just as in the case of warming any body which in the same time loses an equal quantity of heat.

In this way it has already been explained in "1909" p. 18 that different kinds of centra in the same "phosphor" undergo at the same time different increases in temperature, according to the greater or less efficiency of their insulation from communicating energy to

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1) The colour is first green, and then reddish. By projecting a spectrum of the "phosphor" immersed in solidifying hydrogen we have found that the red responsive-glow lies more in the proximate part, the green more in the ultra-red of the spectrum.

the surrounding material. Except for these internal characteristics, the local temperature depends upon the intensity of the ultra-red rays, as we saw just now was the case with the temperature of the surrounding material i.e. of the "phosphor". The following will serve as an example of the dependence of the phenomena upon the two latter circumstances. Ca Bi-"phosphors" prepared specially for this purpose, show next the blue α group, whose permanent phase ranges not far above + 200° C., also a green β band whose permanent phase lies in the neighbourhood of + 300° C. The insulation of the energies of both kinds of centra seems to be practically the same, for when the ultra-red exciting rays are strong enough, it responds first blue, + 200° C., and then green, + 300° C. If the intensity of the ultra-red exciting rays is now small enough only the blue is seen to respond, and apparently the local temperature of + 300° C. can now be no longer reached. Now increasing the intensity of the exciting rays causes the green to appear. When the same experiment was carried out in liquid hydrogen, we were unable even with the most intense ultra-red excitation to get the green to appear; in this case only the blue appeared, and hence the local temperature of + 300° C. cannot be reached when the temperature of the substance is in the neighbourhood of — 250° C.

§ 6. *Spectral distribution of excitation and temperature.*

In a former communication ("1904". p. 471) the supposition was advanced that the excitation-distributions corresponding with the various phosphorescence-bands were independent of the temperature. At that time, however, only the region extending from ordinary to higher temperatures had been investigated. Now, however, in a mixture of carbon dioxide and ether (about — 50° C.), in liquid air (— 180° C.) and in some cases also in liquid hydrogen (— 250° C.) an intense spectrum has been thrown upon the "phosphor" spread out flat, and by this method of illumination the result given above was confirmed. Sr Cu Na, Sr Zn Fl, Ca Mn Na, Ba Cu Li were investigated, the last "phosphor" in liquid hydrogen. Here it appeared that the characteristic excitation-distribution which is shown in Pl. III No. 39 *l.c.*, and which reaches far into the visible region, holds good at that just as at ordinary temperature. In this case the spectrum (from a carbon arc) exciting the phosporescence had to pass through two vacuum glasses (cf. fig. 1.), and by this some of the finer details were necessarily destroyed. In the mixture of solid carbon dioxide and ether and in liquid air, the "phosphors" were enclosed in flat quartz tubes and placed about 1 mm. below the free surface of the bath; the spectrum of a quartz amalgam lamp was then projected upon it from above through a quartz prism; in this way there was less opportunity for disturbance. Here, then, there remains only the great difficulty to which attention has already been drawn ("1904" p. 464.) that the exciting spectrum is discontinuous, so that in a certain measure only the rougher features of the charge distribution always appear, while further finer characteristics must necessarily be obscured by the line-grouping in the spectrum which is used to excite the phosphorescence. It is these rougher features of the excitation distribution — which were already reproduced Pl. III "1904" [1]) — that remain unaltered also at low temperatures.

§ 7. *Momentary and permanent parts of the spectral distribution of excitation.* There had still remained unsolved a question concerning the excitation-distribution in the spectrum which aroused our great interest, and in this respect a new result was obtained.

A characteristic behaviour in the distribution of the exciting power in the case of the clear green head band α of the Sr Cu-"phosphors" had already been noticed ("1904" p. 470; shown graphically by the curves 1 and 2 in fig. 2 and reproduced from Pl. III No. 21 *loc. cit.*); the distribution of the excitation over the spectrum did not disappear regularly, it separated into two spectra, the one quickly (momentarily) increasing and decreasing, the other of much longer duration overlapping this, consisting of completely different groups, and slowly increasing and decreasing. By observing the gradual disappearance, and also the similar increase in intensity, one immediately gains the impression that

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1) One of these excitation-distributions, viz.: that of Ba Cu α_2 (Pl. III. N⁰. 40) must — as has since been discovered — undergo a correction. We intend later to deal in a separate paper with a new investigation of the excitation-distribution by means of a continuous spectrum.

here two different processes proceeding with different velocities overlap, each of which, however, has a different excitation spectrum („1904". p. 470). Then (although mentioning the other view that is now confirmed) the band was regarded as consisting of two coincident bands or of two bands lying very close to each other, $\alpha_1 + \alpha_2$, one of which at ordinary temperature should be in the momentary phase, and the other in the permanent phase, and which, as is always the case with different bands, should each have its own excitation-distribution over the spectrum. The same characteristic of the increasing and decreasing of the excitation-distribution occurring not as a whole as is the case with the Sr Cu α band has later been mentioned by **Werner**[1]) in the case of the Sr Zn α band, and a more detailed investigation of a great number of other bands repeated by P. **Lenard** with better apparatus[2]) than those employed before showed that the above mentioned property is characteristic of all bands, and that it differs in the various bands only quantitatively. As well as these two bands, Ca Mn α_1, Ba Cu α, Ca Bi β are also striking examples of this. The great number of instances observed makes it improbable that in every case one is dealing with the overlapping of bands that lie very close together and are in different temperature phases.

The following observations for which different temperatures were chosen lead to the same conclusion. The observations at low temperatures were made according to the method already described; for those at higher temperatures and up to the beginning of red heat, the "phosphor" enclosed in a flat quartz tube was placed in a hot-air bath and illuminated by a spectrum. From these experiments it appeared that those parts of the spectrum to whose excitation momentary response was given and which we shall call collectively the "momentary part", *remained* momentary as far as low temperatures up to those of liquid air[3]) were concerned at *all* temperatures, while those portions of the

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1) A. **Werner**. Dissert. Kiel. July 1907; Ann. Phys. 24. p. 190, (1907).

2) Which were rendered available by the establishment of the Radiological Institute at Heidelberg.

3) In liquid hydrogen the observation as already indicated § 6 proved too difficult.

spectrum which induced an afterglow, the "permanent part", induced this afterglow only within the temperature range of the permanent phase for the band in question, as was to be expected. At the temperatures of the upper or of the lower momentary phases also the „permanent part" becomes momentary in accordance with the properties of this phase.

It is especially worth noting that whenever the bands are in the permanent phase, the particular momentary part overlapping the "permanent part" nevertheless remains unchanged, so that when a band is excited even at temperatures within the permanent phase, the two processes which we have called "momentary" and "permanent" proceed simultaneously [1]) in such a way that the quantitative relation between the two processes differs according to the exciting wave-length. Some wave-lengths induce almost the momentary process alone, others almost only the permanent process; in general, any wave-length will induce both processes at the same time. For instance, $\lambda = 400 \mu\mu$ excites Sr Cu α momentarily, $\lambda = 434 \mu\mu$ permanently; $\lambda = 200 \mu\mu$ and $\lambda = 450 \mu\mu$ excite Sr Zn α momentarily, $\lambda = 366 \mu\mu$ permanently; in the same way $\lambda = 200 \mu\mu$ excites Ca Mn α momentarily and $\lambda = 334 \mu\mu$ permanently. The general characteristic of the excitation-distribution is that the shortest wave-length (in the extreme ultra-violet) induces only the momentary process, and that towards the limit of the excitation-distribution on the side of the greater wave-lengths continuous and momentary excitation interchange periodically one or more times [2]).

If the permanent part in the afterglow is to be well observed, illumination must be continued for several minutes with a very intense spectrum, for it has always appeared from the experiments that a powerful ("1904" p. 477) and also a prolonged ("1904" p. 281) illumination is necessary to excite permanent emission to the full. If the illumination has not been sufficiently prolonged, or has been performed with a spectrum that was not sufficiently intense, it can happen that places of moderate duration will at first show a clearer afterglow than places of maximum duration because the latter had not yet been sufficiently excited.

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[1]) This point has already been elucidated particularly with reference to the Sr Cu α band ("1904", p. 668). By special measurements A. WERNER has demonstrated it for the Sr Zn α band.

[2]) A separate communication will deal with these characteristics.

As has already been said, the momentary part always seemed to overlap the permanent part, sought for in this way. The former can be observed during the first illumination with the spectrum, or better still, in that part of the phosphorescent light which quickly disappears immediately after the illumination ceases. The momentary glow that was to be observed in these parts of the momentary portion, *e.g.* in the extreme violet, showed in all cases the character of the *upper momentary* phase, that is to say, there was no storing of electrons; parts illuminated by this portion of the spectrum cannot be made to glow either by warming or by ultra-red excitation, only those parts of the spectrum which belong to the permanent part will induce a glow.

There are thus definite wave-lengths which in all temperature phases of the centra bring into action the momentary process exclusively, or almost so; that is to say, the electrons that under the photoelectric influence of these wave-lengths are ejected from the metallic atoms of the centra return quickly to their metallic atoms, giving out light, while at the same time other wave-lengths cause electrons to be ejected from the metallic atoms of the same kind of centra, and these electrons are retained in the neighbourhood (storing, process of afterglowing). *This circumstance can be ascribed to the fact that the ejection from the metallic atoms caused by the various wave-lengths takes place in different directions in space (fixed in the atom), and therefore also in different directions with regard to the neighbouring atoms of the centrum*, the atoms of the alkaline earth metal, the sulphur atoms, perhaps also atoms coming from the additional substance.

Only those electrons which are directed towards places in the neighbourhood suitable for retaining electrons, are retained and stored, thus causing the permanent phase as the temperature falls within the region of permanency. It has already been indicated where these places must be looked for whose presence makes storing possible. It has already been shown in "1904" that they can only be places *within* that molecule to which the name "centrum" has been given. "For every band (kind of centrum) even of the same "phosphor" stores ("1904" p. 473 and seq. p. 481) up its own excitation in such a manner that it cannot be used by any other band [1])", and also the storing of electrons (the permanent phase) in the different bands of the same „phosphor" is often bound at widely differing temperatures ("1904" p. 761); this has also been further confirmed by our experiments at the lowest temperatures. The material surrounding the centra, which is the same for all kinds of centra in the same "phosphor", cannot therefore have anything to do with the accumulation of electrons, only the molecule called the centrum can play a part in that process.

At first there seemed to be some foundation for the supposition that atoms that had passed over from the surrounding material to the centrum would be able to cause storing of electrons. If, however, the result that has begun to appear probable from the more detailed investigations of P. LENARD, viz. that the additional substance has no influence upon the intensity nor, *independent* of that circumstance, upon the duration of the bands, will be confirmed, then in the first place the sulphur atoms in the centra are to be taken into account as responsible for the efficient and lengthy storing of electrons. For it is only substances containing sulphur, "phospors" of the alkaline earths, and zinc sulphide, that show persistent phosphorescence.

Whatever those places in the molecule which we have called centrum may be which have the power of storing electrons, we shall begin by accepting, for trying an explanation, that the electron which is ejected from the metallic atom must in every case reach one of those places before it can be retained. By no means every wave-length of the exciting light seems suitable for this purpose. But not even the most suitable wave-lengths, corresponding with the places of maximum duration in the excitation-distribution, can in consequence of the heat motions of the molecules of the "phosphors" and their atoms that cause the individual centra to simultaneously assume different configurations, be the most suitable for *all* centra *at the same time* for ejecting the electron just in the direction of the place in which it can be stored.

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[1] See also the comprehensive résumé "1909" p. 14. In P. LENARD and SEM SAELAND, Ann. d. Phys. 28. (1909). "the surrounding of the centrum" is inadvertently spoken of twice instead of "the surrounding of the metallic atoms" as the place where the electrons are stored.

This is the explanation of the circumstance that in "1904" (p. 281, 477, 475) it was found, that in order to develop the afterglow to the full and in the same manner to have good storing of electrons in the lower momentary phase long exposure to, or at least great intensity of the exciting light was necessary. For duration and intensity both increase the number of electrons ejected from the metallic atom (after intermediate returns), and thus also increase the probability that amongst these there will be found some whose direction is the proper one. In the same way, it can be explained that the momentary process, the glow during the illumination without afterglow, in the lower momentary phase is not entirely wanting in the permanent part, for it is just the return of the electrons which have not reached the place where they are stored that causes this glow.

§ 8. *Non-resolution of bands in amorphous substances.* The supposition that in consequence of heat motions the atoms of the centra temporarily assume different configurations also an affords explanation of the broadening and narrowing of the emission bands at high and low temperatures respectively, analogous to that given by P. Lenard in explanation of the broadening of the metal-lines in flame-spectra [1]), and to that given by H. and J. Becquerel and H. Kamerlingh Onnes at the end of their paper for the modification of the positions of the bands of uranyl under the influence of the proximity of other atoms which go with it to form a molecule. For the different configurations will cause varying changes in the periods of the inherent vibrations of the centra. Without heat motion, at 0° K., each centrum would have a definite time of vibration, invariable with the time. It still depends, however, upon a particular circumstance whether these inherent and time independent vibration periods of all centra (of the same

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1) P. Lenard. Ann. d. Phys. 17 p. 232. 1905.

kind) in the whole preparation should in each case be constant, which would be necessary in order to obtain a spectrum consisting of fine lines. For this all centra would have to take up the same position with respect to the neighbouring molecules. For these molecules in a solid substance act with different forces upon the centra according to their distances and orientation, and these must cause different modifications in the period. These equal distances and resulting equal periods for all parts of the preparation independent of time *and* position are to be expected only in crystalline substances such as those investigated by the above-mentioned experimenters, and not in the amorphous "phosphors" investigated by us; this affords an explanation of the fact that even at 14° K. we did not yet see the spectra resolved into lines. What we saw was — according to the image just developed — the overlapping of bands consisting of the sharp lines which each centrum gives at very low temperatures, and which by mutual interaction become less sharply defined. The same remark may be applied to the excitation- and extinction-distributions ¹).

§ 9. *On the upper temperature limits to the excitation of phosphorescence by light, and on the glow of "phosphors" when heated in flames, or when crushed at high temperature.* It seems of importance to us to remark that our demonstration of the existence of phosphorescence, and particularly of the storing of electrons when the temperature sinks to 14° K., also taken in connection with an earlier research ²), affords a proof that the photoelectric action at low temperatures remains unchanged even down to this very low temperature. This proof was first given by LIENHOP ³), of the Kiel Laboratory, for temperatures sinking to close upon that of liquid air, from which the validity for all temperatures followed with the highest probability; and for high temperatures MILLIKAN and WINCHESTER ⁴) and LADENBURG ⁵) have given important direct confirmations It

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1) The latter according to "1909" should offer the first chance of the resolution into a group of lines.

2) P. LENARD and SEM SAELAND: Ann. d. Phys. 28. p. 476. (1909).

3) A. LIENHOP: Ann. d. Phys. 21. p. 211. (1906).

4) MILLIKAN and WINCHESTER: Phil. Mag. July 1907.

5) E. LADENBURG: Verh. d. D. Phys. Ges 9. p. 165. 1907.

seems therefore to be beyond doubt that the ejection of electrons by atoms in response to excitation by suitable wave-lengths takes place at all temperatures; and it must, therefore, be explained why the phosphorescence in response to light excitation of the alkaline earths cannot be noticed above a definite high temperature.

It has already been shown that this upper limit to the induction of phosphorescence by light lies lowest in the Ba-"phosphors" and higher in the Sr- and Ca-"phosphors" -- *e.g.* in Ba Bi β at 170° C., in Sr Bi β above 300° C., and in Ca Bi β a little above 500° C.-- and that it, however, is in no case a sharply defined temperature, but that at high temperatures the excitability by light slowly ceases ("1904", p. 452). The observation has later been added [1]) that it is just in the neighbourhood of this limit of temperature that the "phoshors" begin to conduct electricity. If we assume that this conduction is electrolytic, then it is an obvious deduction that the presence of electrolytic ions prevents the excitation of phosphorescence by light, perhaps through the circumstance that the lost electrons are brought back to the metallic atoms which have been rendered positive by their ejection of electrons under photo-electric influence, not as free electrons, but by anions, and it must then be assumed of this kind of neutralisation, that it is not accompanied by emission of light. If the "phosphor" is in a medium containing many free electrons, such as *e.g.* a flame [2]), then it appears to be able to phosphoresce far above that temperature limit; it lights up of its own accord with the phosphorescence colour belonging to this temperature, while light at this temperature is not necessary to induce phosphorescence, and indeed could not do so. To this group of phenomena also belongs that described in "1904" of the "phosphor's" lighting up with colours, when after being freshly prepared and still glowing with heat, they are crushed by pressure In that case there always occurs a burning of the sulphur from the "phosphor" by contact with the air; in fact this glow is seen only where fresh cleavage surfaces formed in the crushing come in contact with the air, and there also small sulphur flames are often to be seen. If too rapid

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1) P. Lenard and Sem Saeland. Ann. d. Phys. 28, p. 498. 1909.

2) P. Lenard. Ann. d. Phys. 9, p. 649. 1902.

cooling is prevented, addition of oxygen increases the glow. If the "phosphor" is too cold to show the phenomenon of the burning away of the sulphur, then also breakage causes no glow.

On the other hand by holding it on a platinum wire in a flame one can easily keep a piece of "phosphor" — *e. g.* Ca Bi Na or Sr Bi Na — that has not previously been under the influence of light, glowing for a long time with its phosphorescence colour (heat band) at a red heat, and therefore above the temperature limit at which it could be excited by light. The flame must be poor in oxygen if the phenomenon is to last, for as soon as the "phosphor" is deprived of sulphur by burning, the glowing ceases.

We further remark that according to the theory above developed the upper temperature limit of phosphorescence excited by light seems to be a consequence of the electrolytic dissociation of the material of the "phosphor", while its entering the upper momentary phase — which happens for the different bands even of the same "phosphor" at such widely differing temperatures, *e.g.* a little above — 180° C. for Ca Bi γ, and at + 450° C. for Ca Bi β — can depend only upon processes within the corresponding centrum, that is to say, upon the rendering of electrons from the place where they have been stored in the centrum occurring at temperatures differing widely according to the nature of the centrum.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

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H. KAMERLINGH ONNES. "Isotherms of monatomic gases and their binary mixtures. III. Data concerning neon and helium."

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H. KAMERLINGH ONNES. "*Isotherms of monatomic gases and their binary mixtures.* III. *Data concerning neon and helium.*"

§ 1. *Critical pressure and triple-point pressure of neon.*

Mr. G. Claude of Paris had with extreme kindness placed at my disposal a considerable quantity of a gas rich in neon which had been obtained by fractional distillation of air, carried out by the Paris Société de l'Air-liquide according to Claude's method. By means of my hydrogen circulation I was in a position to prepare from this a quantity of pure neon quite sufficient for the determination of various physical properties of this gas which up to the present, has been but little investigated. When the pure neon was first collected in the mercury pump, a characteristic light phenomenon was at once apparent; this phenomenon seemed to have been unknown up till that time, although, as appeared from a paper shortly afterwards published, it had been observed by Prof. Collie, who also was indebted to the kindness of Mr. Claude, and had been further investigated by him. The phenomenon is this: — whenever the mercury sinks from the reservoir of the Töpler-pump to the lower tube, the meniscus is surrounded at the contact with the glass, by a narrow ring of clear orange light. By this neon can be immediately recognised.

The triple-point pressure and the critical pressure were determined in the following manner. Pure neon was condensed in a glass tube which a steel capillary connected with a manometer tube and a valve through which gas from a reservoir could be admitted. The condensation was easily brought about by immersing in liquid hydrogen the experimental tube, surrounded by a protecting tube that served to lessen heat-conduction and thus to delay the temperature changes in the contents of the tube. Then by allowing the neon to flow quickly into the apparatus it was obtained in the liquid state in the experimental tube. If the protecting tube is kept surrounded by liquid hydrogen, then the experimental tube cools slowly, and after a time the neon begins to solidify. If, on the other hand, the liquid hydrogen surrounding the protecting tube is sucked away the temperature of the experimental tube slowly rises, and if, by means of the valve, the quantity of neon in the tube is well regulated, the meniscus is seen to disappear somewhere in the tube. By allowing the gas to expand through the valve the meniscus can be made to re-appear in the middle of a mist, just as it happens in ordinary determinations of the critical state. When the meniscus disappeared the critical pressure was read on the manometer tube attached to the experimental tube.

For the triple-point pressure was found 35 c.m. and for the critical pressure 29 atmospheres.

A bath of liquid neon would therefore prove of great advantage in investigations in the neighbourhood of the critical point of hydrogen. I hope to be in a position to make use of such a bath through the further kindness of Mr. CLAUDE, to whom I now express my warmest gratitude for the help already given.

§ 2. *Critical pressure of helium. Lowest temperature reached.*

In the first liquefaction of helium I made use of a very provisional estimation of the critical pressure giving a value of 7 atm. The observation of the vapour-pressure and the density of liquid helium showed that the critical pressure must be much lower and must lie rather between 2 and 3 atmospheres.

If this value had been taken, then a lower value would also have been chosen for the pressure under which the gas to be liquefied was pumped through the regenerator spiral. That there was, in fact, occasion for this was shown by the circumstance that in the actual experiment the expansion pressure was lowered with successful result. Indeed, had account not been taken of a warming effect that was observed and of the knowledge that the JOULE-KELVIN process can give a warming if the pressure is too high even when the temperature is suitable for the production of liquid the experiment might perhaps have been unsuccessful; and the failure might have been attributed to a very special deviation of helium from the law of corresponding states, and hence to the expansion pressure not being sufficiently high, or to an error in the estimation of the critical temperature.

When, therefore, a further liquefaction of helium was proceeded with [1]) (which had been delayed by various circumstances for a considerable time) the pressure in the regenerator spiral was from the beginning brought to a value of 50 atmospheres. With this the liquefaction proceeded as well as could be desired. To keep the circulation in action once the liquid was formed, it seemed advantageous to bring the pressure in the regenerator-spiral even to the still lower value of 20 atmospheres. Just as has already been remarked, now that the conditions for the liquefaction of helium are known, the repetition of the experiment with the same apparatus and the keeping of 60 c.c. of liquid helium in it for several hours has become a work that offers no serious difficulty, although it necessitates much exacting preparation. And now a further stap can be attempted, and the liquid helium poured off into a cryostat in which various measuring apparatus can be immersed.

In the new experiment I have been successful in still further lowering the temperature of the liquid helium. It was definitely known that in the first experiment the vapour pressure was lowered to 1 c.m., and that the helium was still liquid at that pressure; now I have successfully lowered the pressure to 2.2 m.m. Even at that pressure the helium remains a light mobile liquid. When lowered to this low temperature it shows considerable shrinkage, and, in correspondence with the greater density clearly shows a rise against the wall of the glass [2]). The temperature which is reached by thus strongly cooling the liquid helium may be estimated to lie below 2°.5 K., perhaps at 2° K.

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[1]) In the first repetition of the experiment we did not succeed in preventing the formation of a slight deposit on the hydrogen glass. Had this been the case to the same extent in the first experiment, then there had been every probability that, on account of the first observation of the liquid helium being much more difficult, the experiment had been abandoned as unsuccessful, while as a matter of fact, the apparatus contained liquid helium.

[2]) In the former communication it was said that the meniscus at the boiling point stands out against the wall as sharp as a knife. And, indeed, this reproduces in the best way the first impression which the meniscus makes. Proper illumination, however, even under these circumstances, succeeded in making visible an extremely slight rise of the liquid against the wall of the vessel.

I have tried in the new experiment to measure these extremely low temperatures with the gas-thermometer. It must, however, be remarked that when the temperature sinks so low, the thermometer may be used only so long as the pressure of the helium in the thermometer remains lower than the vapour pressure of the liquid helium, and when the latter is 2 m.m. the pressure in the thermometer at that temperature must be still lower, *e.g.* 1 m.m. The pressure at which the thermometer is filled at ordinary temperature is therefore taken not higher than 100 m.m. The difficulties of determinations with this very special gas-thermometer in the immediate vicinity of the helium apparatus have not yet been quite overcome, and hence further information concerning the temperature cannot yet be given.

We can, however, already announce a first experimental determination of the critical pressure: it gave 2.75 atmospheres. While an estimate formed from the observations with liquid helium showed that the estimated value on which the liquefaction experiment was based was much too high, it now seems to show a deviation in the other direction, viz. it gives too low a value for the critical pressure. Until a cryostat is obtained suitable for such temperatures as here come into account, 2.75 atm. can be regarded only as a provisional value, and it is perhaps better to round it off to 3 atmospheres.

In the meantime the value obtained in connection with more recent determinations which bring the boiling point still closer to 4° K. confirms the estimate of the critical temperature as being at 5° K. But as has already been mentioned, determinations concerning temperatures and densities will be reserved for a later communication.

The determination of the critical pressure took place practically in the same manner as that of neon. It was done in a small pyknometer, a vessel of 0.5 c.c. capacity with a narrow graduated stem, that was placed along with the reservoir of the helium thermometer (see Comm. N°. 108) in that part of the liquefier destined for the reception of the liquid helium; it was attached to a steel capillary and came outside the apparatus just as the capillary of the helium thermometer. This capillary was then connected with a manometer tube, an admission valve, and a reservoir, just as with neon. (See § 1).

According as the level of the liquid helium in the liquefier was more or less lowered [1]), this pyknometer was partially or wholly immersed in the liquid helium, or came wholly above it; helium from the reservoir connected with the pyknometer could be condensed in it, so that the meniscus could be seen in it or in its graduated stem. For density determinations the quàntity of helium admitted to the pyknometer was so regulated that the position of the meniscus upon the graduated stem could be accurately determined, while for determinations of the critical pressure the vaporisation was followed while the meniscus was lowering in the pyknometer. The critical pressure was read at the moment when the meniscus when standing half-way up the pyknometer reservoir disappeared, when the helium surrounding it was sufficiently vaporised. The meniscus could be brought back again for a short time by expansion.

The estimate that temperatures below 2°.5 K. have already been reached depends also upon the critical pressure given. An attempt will be made to reach still lower temperatures by causing the helium to evaporate from still lower pressures; for this purpose the apparatus in which the helium is to be cooled by being allowed to evaporate under pressures still lower than 2 m.m. will be surrounded by a layer of liquid helium to protect it from conduction of heat, and to prevent the formation of unmanageable volumes of vapour.

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[1]) This was brought about by allowing insufficiently cooled helium to blow through the regenerator spiral into the helium liquefier.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 113.

ERNST COHEN and **J. OLIE Jr.** "The atomic volume of allotropic modifications at very low temperatures." (*With a plate.*)
(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, **30 October 1909**, pp. 377—385.)

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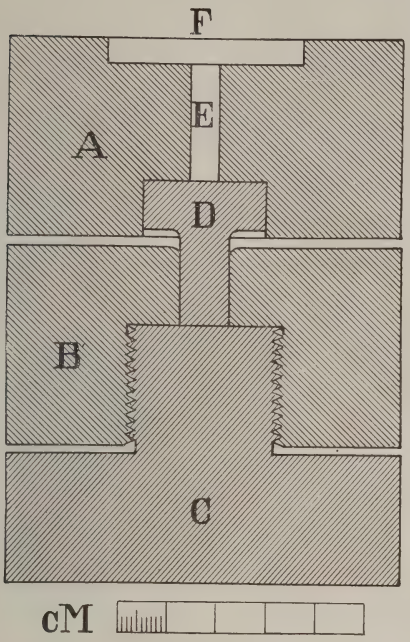
ERNST COHEN and **J. OLIE Jr.** "The atomic volume of allotropic modifications at very low temperatures".



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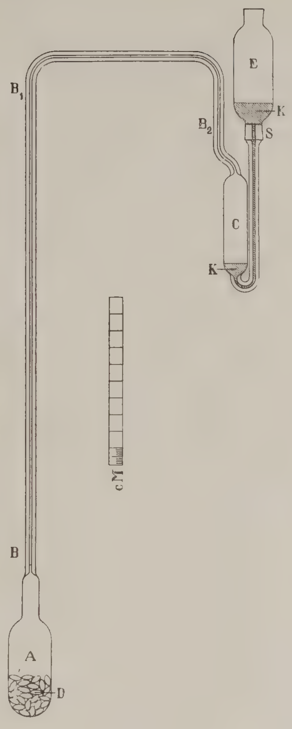

Fig. 2.

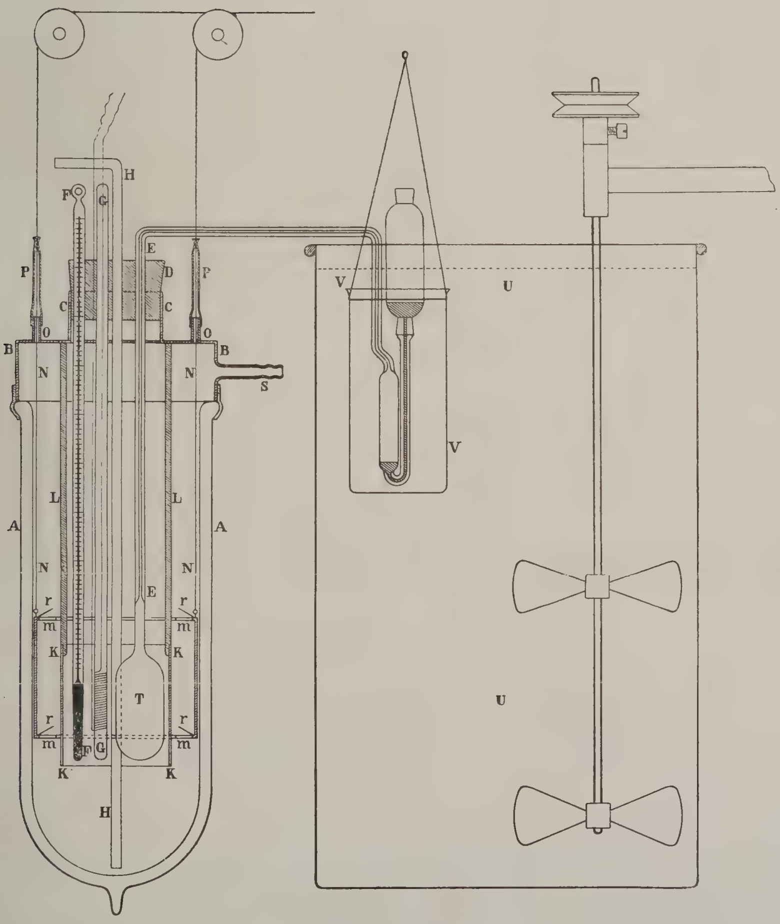

Fig. 3.

Communication No. 113.

ERNST COHEN and J. OLIE Jr. "*The atomic volume of allotropie modifications at very low temperatures.*"

1. In the discussion on a communication: "The allotropic forms of silver and gold", made by one of us in the meeting of the Deutsche Bunsengesellschaft at Dresden [1]) the question was raised whether the atomic volumes of the different allotropic modifications of a certain element become equal at the absolute zero point. As the answer to this question, which can only be given by experiment, is in the closest connection with some other points concerning the periodic system of the elements to which we shall come back later on, we have carried out an investigation in the above mentioned direction, which may be briefly described here [2]).

2. We have carried out our measurements only with diamond and graphite, and with white and gray tin, as a preliminary investigation showed us, that the allotropic forms of phosphorus were less suitable.

3. Through the kindness of Mr. S. LEHMANS at Amsterdam Mr. LOUIS TAS placed ten grammes of diamond (314 pieces) at our disposal. We may be allowed here also to express our hearty thanks to them.

4. Mr. P. LEBEAU of Paris sent us a large quantity of graphite, made by the late HENRI MOISSAN; on investigation this preparation appeared to be very pure.

As the researches of LE CHATELIER and WOLOGDINE [3]) have shown that graphite assumes a sharply defined specific gravity at a certain temperature only when it has been exposed to great pressures (according to the above writers inclosed gases are expelled from it in this way) we have exposed our preparation to pressures of 5000—10000 atms., and have not used it until the spec grav. remained constant after repeated compression.

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[1]) Zeitschrift für Elektrochemie 21, p. 589 (1906).

[2]) The full discussion will shortly appear in the Zeitschrift für physik. Chemie.

[3]) C. R. 146, p. 49 (1908).

We made use of an apparatus constructed specially for this purpose, which is reproduced in fig. 1. In the steel block *B* a hole is bored, into which powdered graphite is put. In this hole fits the steel piece *D*, which is pressed down by means of the block *A* under an hydraulic press. The graphite cylinder made in this way may be easily removed from *B*, if *C* is unscrewed, and may then be pushed from the hole by means of the piece *FE*.

5. The white tin, which was used in our measurements, was the same preparation that served in the investigations of ERNST COHEN and E. GOLDSCHMIDT [1]; the gray tin came from a block of Banka tin, which on a former occasion had been kindly presented to us by Mr. H. BAUCKE, chemical engineer [2]). On investigation this material proved to be very pure. By a special investigation we convinced ourselves that it did not contain any white tin.

DETERMINATION OF THE SPECIFIC GRAVITY.

6. Our determinations were carried out at 18°, —38°, and — 164°.

A. *Measurements at* 18°.0.

7. For this purpose we made use of a pycnometer. As graphite is not moistened by water, we took toluene as filling liquid. In connection with this the ground-glass stopper of the pycnometer was made very long. Our apparatus had a capacity of ± 22 cc.; it was gauged by means of water carefully freed from gases by boiling. The weighings were carried out on a balance, on which $^1/_{10}$mg. could be read. All weighings were reduced to vacuum; the densities were expressed in the density of water at 4°.0 as unit.

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[1]) Zeitschrift für physik. Chem. 50, p. 225 (1905).

[2]) Zeitschrift für physik. Chem. 63, p. 625 (1908).

After the substance which was to be examined, had been introduced into the pycnometer, the latter was filled with toluene, and connected with the air pump. When the toluene had boiled for some time, the pycnometer was again filled up with that liquid, and placed in a thermostat, which was kept at 18° 0. The thermometers used were tested by a normal thermometer (divided into $^1/_{10}$°), which had been tested by the Physikalisch-Technische Reichsanstalt at Charlottenburg.

The stopper of the pycnometer had a capillary bore; the upper surface of the capillary was made opaque by grinding. As soon as this upper surface remained perfectly dry for ten minutes, the liquid was sucked off by means of a capillary pipette down to a mark on the capillary of the pycnometer. Then the pycnometer was removed from the thermostat, and weighed after having been carefully dried. All the determinations were made twice.

For the toluene used we found: $d\,\frac{18^\circ.0}{4^\circ.0}$ **0,8666**.

Table I contains the results of the determinations at 18°.0.

TABLE 1[1])

Temperature 18°.0.

Substance.		Weight of the expelled toluene in gr.	Weight of the expelled water in gr.	$d.\frac{18^\circ.0}{4^\circ.0}$	Remarks.
Name.	Weight in gr.				
Diamond	9.9790*	—	2.8296*	3.514	
Graphite	8.4424*	3.2961*	—	2.217	
Graphite	8.5504*	3.3412*	—	2.215	
White tin	16.8488	—	2.3082	7.281	prepar. from gray tin
White tin	23.7052*	—	3.2458*	7.285	» from melted tin
Gray tin	33.4100*	—	5.7953*	5.751	fine powder
Gray tin	29.9170	—	5.1789	5.763	coarser »

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[1]) The values in this table marked with an * have served in the further calculations.

B. *Measurements at low temperatures.*

8. As far as we know an accurate method of determining the specific gravities of solid substances at very low temperatures does not exist yet [1]), we therefore had in the first place to devise one.

Our method may be considered as a combination of the dilatometer and the weight-thermometer.

It appeared at the outset that we could extend our experiments no further than — 164°. For no liquid is known as yet which remains sufficiently fluid below that temperature. Pentane e. g. (socalled Pentan für Thermometer) becomes so viscous some few degrees lower, that it is of no use whatever.

a. *The dilatometer.*

9. Our dilatometer (Fig. 2) was made of Jena glass 16^{III}, as the coefficient of expansion of this kind of glass at very low temperature is sufficiently known through the investigations of KAMERLINGH ONNES and CLAY.

A is a reservoir of a capacity of ± 20 cc.; the capillary BB_1B_2 has a bore of 0.7 mm.; the capacity of C is ± 6 cc., that of E ± 20 cc.

By the aid of a ground-glass junction S, E could be placed on the capillary tube. This has the same bore as BB_1B_2.

The course of the experiment is now as follows:

After A has been cleaned, and weighed, the substance which is to be examined as to its specific gravity, is introduced, and the whole is weighed again. The tube BB_1B_2 is fused on to it, and the whole weighed again. Then a mark is etched on the capillary BB_1B_2, just below the place where the level of the cooling liquid will ultimately be. A is filled with pentane up to this mark, after it has been brought to 18°.0 in a thermostat. It is weighed again.

Now A is put into a refrigerating mixture, and the other part of the apparatus is fused to the capillary at B_2.

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[1]) The determinations made by DEWAR, Chemical News 85, p. 289 (1902), were of a more preliminary character. His method was altogether unsuitable for our purpose as it is not sufficiently accurate.

E is connected with a three-way tap (*not* greased), which enables us to exhaust the apparatus, and to fill it up with pentane. These manipulations are repeated a few times.

If in this way the apparatus has been filled with pentane to about halfway the height of E, we pour pure, doubly distilled mercury into E by means of a funnel. We remove the excess of pentane by exhausting once more, so that the mercury at last penetrates into the bottom part of C, and KS remains filled with it.

ABB_1 is placed in the cryostat, and B_2CSE in a thermostat U (fig. 3), which is kept at 18°.0.

The mercury now rises in C; mercury is poured into E, so that, when A has assumed the temperature of the cryostat, the mercury in E stands a few centimeters above the ground-glass junction.

If the temperature of the cryostat has remained perfectly constant for an hour (the temperature is determined by means of a resistance thermometer), E is removed. The excess of mercury in E, is then received in a glass beaker V (fig. 3). If the capillary remains quite filled to the top, the vessel E is again placed on the ground-glass junction after having been carefully cleaned beforehand, and now the temperature of ABB_1 is slowly raised. The mercury that issues at S, is received in E. After some time the whole apparatus is placed in the thermostat of 18°.0, and there it is left for a considerable time. Now a glass beaker is placed under B_1CSE, E is carefully removed from the ground-glass junction, so that the mercury flows into the beaker, the mercury on the surface of the ground junction being collected with a feather.

The mercury found in the beaker is carefully washed with water, then with alcohol. This is removed by means of a current of air which has been filtered through cotton wool. The drying is repeated, till the weight has become constant.

b. *The Cryostat.*

10. For the measurements at — 38° we used liquid methyl chloride under reduced pressure, at — 164° liquid methane at 1 atm. The apparatus constructed by KAMERLINGH ONNES for such purposes (Comm. No. 94*c*), is diagrammatically represented in fig. 3.

AA is an entirely transparent vacuum glass, which can contain ± 2 liters of liquid, *BB* is a brass cover, which can be fastened gastight on the glass by means of a rubber ring. The neck *CC* can be closed gastight by means of a large rubber stopper. The stopper *D* was pierced in six places; through three holes passed the capillaries *E* of three dilatometers. Moreover the glass vessel *AA* was provided with a resistance thermometer *G*, a pentane thermometer *F*, and a glass tube *H*. The last reached to the bottom of the vacuum glass.

The reservoirs *T* of the dilatometers were surrounded by a protecting jacket *KKKK* of nickel plate. This jacket was supported by the nickel bars *LL*. The liquid gas was kept in violent motion by the stirrer *mmmm*. The valves *rrrr* promote the stirring in a high degree. The stirrer is suspended on three wires *NN*, which pass airtight through the cover *BB*. To satisfy this condition they pass through the metal tubes *OO*, and through the rubber tubes *PP*; in the latter the wires are fastened airtight. By means of an electromotor the wires are brought in an upward and downward motion.

The liquid gas was pumped into the vacuum glass by means of the tube *HH*.

When we worked under reduced pressure, *S* was connected with the air pump.

11. The tables 2—9 contain the results of the measurements, which are used in the calculation.

TABLE 2.

Temperature 18°.0.

The dilatometer contains	Weight of the solid substance in gr.	Weight of the pentane in gr.	Number of the dilatometer.
Diamond—Pentane	9.9790	12.0820	I
Graphite—Pentane	8.7954	11.6135	II
White tin—Pentane	23.7026	12.7496	III
Gray tin—Pentane	26.4843	10.5339	IV
Pentane	—	12.8847	V
Water	—	20.2058	V

TABLE 3.
Temperature —163°.6.

Number of the dilatometer.	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0.
I	Diamond—Pentane	67.5817
II	Graphite—Pentane	65.0153
V	Pentane	72.1680

TABLE 4.
Temperature — 163°.2.

Number of the dilatometer.	The dilatometer contains	Weight in gr. of the mercury thas has flowed out at 18°.0
I	Diamond—Pentane	67.6155
II	Graphite—Pentane	65.0644
V	Pentane	72.2079

TABLE 5.
Temperature —163°.5.

Number of the dilatometer.	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0
I	Diamond—Pentane	67.5664
II	Graphite—Pentane	65.0778
V	Pentane	72.2685

TABLE 6.
Temperature —38°.0.

Number of the dilatometer.	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0
I	Diamond—Pentane	21.2138
II	Graphite—Pentane	20.4593
V	Pentane	22.7002

TABLE 7.

Temperature —37°.75.

Number of the dilatometer.	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0
I	Diamond—Pentane	21.1658
II	Graphite—Pentane	20.3958
V	Pentane	22.6509

TABLE 8.

Temperature —163°.3.

Number of the dilatometer.	The dilatometer contains	Weight in gr. of the mercury that has flowed out at 18°.0
III	White tin—Pentane	71.7180
IV	Gray tin—Pentane	58.9882
V	Pentane	72.2378

TABLE 9.

Temperature —163°.4.

Number of the dilatometer.	The dilatometer contains	Weight in gr. of the mercury thas has flowed out at 18°.0
III	White tin—Pentane	71.7131
IV	Gray tin—Pentane	58.9744
V	Pentane	72.2318

12. The calculation of the experiments may be summarized here as follows: if we call:

P_d the weight of the diamond used;

$P^{Ip}_{18^\circ.0}$ the weight of the pentane at 18°.0, in the dilatometer I with the diamond;

$P^{V}_{18^\circ.0}$ the weight of the pentane, in the dilatometer V at 18°.0;

U_p the weight of the mercury which has flowed out during the heating of dilatometer V (filled with pentane) from $-t°$ to $18°.0$;

$S_{18°.0}$ the specific gravity of mercury at 18°.0;

$W^{d}_{18°.0}$ the weight of the water that is expelled by the diamond at 18°.0;

$D^{w}_{18°.0}$ the density of water at 18°.0;

δ the mean coefficient of expansion of the (Jena) glass from 18° to $-t°$;

U_d the weight of the mercury which has flowed from dilatometer I, when it is heated from $-t°$ to 18°.0, then the specific gravity of diamond at $-t°$ is

$$S_{-t°} = \frac{P_d}{\dfrac{P^{Ip}_{18°.0}}{P^{V}_{18°.0}} \; \dfrac{U_p}{S_{18°.0}} + \dfrac{W^{d}_{18°.0}}{D^{w}_{18°.0}} \{1-\delta(t+18)\} - \dfrac{U_d}{S_{18°.0}}}.$$

Table 10 has been calculated by means of this expression (resp by means of the analogous expressions for the other substances investigated).

TABLE 10.

Temperature t	Spec. gravity $d\frac{t}{4°.0}$			
	Diamond	Graphite	White tin	Gray tin
— 163°.6	3.519	2.223		
— 163°.2	3.518	2.224		
— 163°.5	3.509	2.222		
— 163°.3			7.350	5.768
— 163°.3			7.351	5.768
— 38°.0	3.510	2.217		
— 37°.75	3.510	2.217		
+ 18°.0	3.514	2.216	7.285	5.751

13. Finally table 11 gives a survey of the ratio of the spec. gravities of different allotropic forms of the same element at different temperatures:

TABLE 11.

Temperature	Ratio $\frac{S_{\text{diamond}}}{S_{\text{graphite}}}$	Ratio $\frac{S_{\text{white tin}}}{S_{\text{gray tin}}}$
+ 18°.0	1.585	1.266
— 38°	1.583	
— 164°	1.582	1.274

14. We see from table 11 that down to — 164° there are no indications that the spec. gravities (resp. the spec. volumes) of the different allotropic modifications of the same element converge to one and the same value in approaching the absolute zero point.

It is only owing to the great kindness of Prof. KAMERLINGH ONNES, who placed the resources of his laboratory at our disposal, that it has been possible for us to carry out the above investigation. We may be allowed here also to express our great indebtedness to him.

To Mr. G. J. FLIM, technical assistant at the Cryogenic Laboratory at Leiden, many thanks are due for his intelligent assistance.

October 1909.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 114.

PIERRE WEISS and **H. KAMERLINGH ONNES.** "Researches on magnetization at very low temperatures." (*With two plates*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* 26 Februari 1910 pp. 768—796.)

EDUARD IJDO — PRINTER — LEIDEN.

PIERRE WEISS and H. KAMERLINGH ONNES. "Researches on magnetization at very low temperatures".

PLATE I.

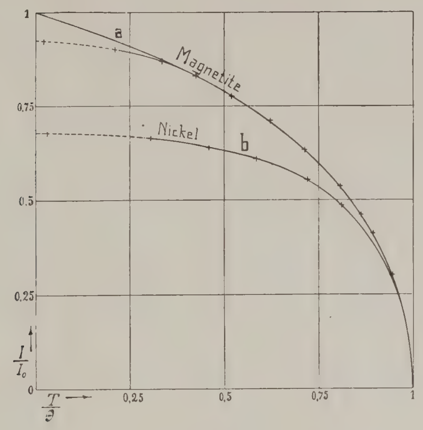

Fig. 1.

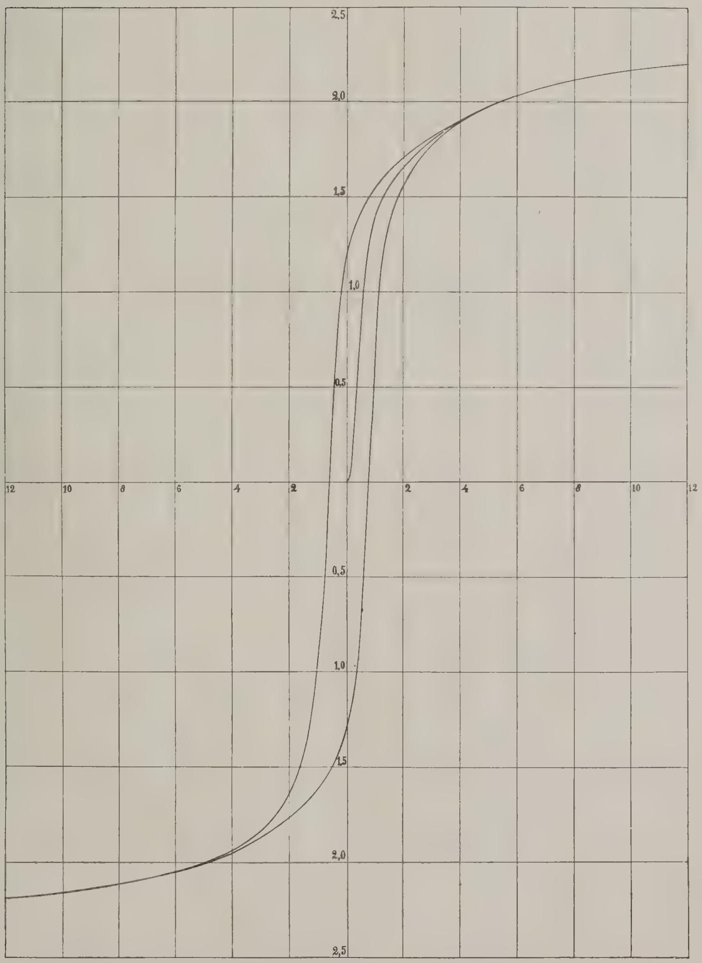

Fig. 2.

Communication No. 114.

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PLATE II.

Fig. 1.

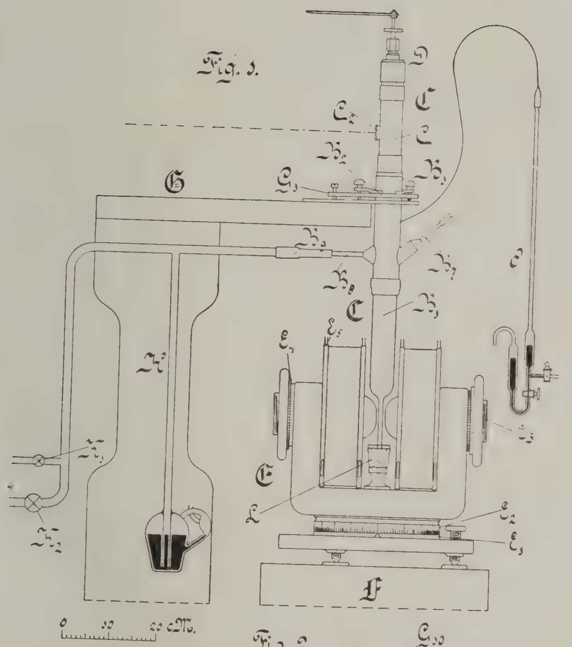
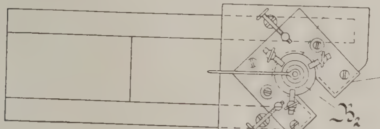
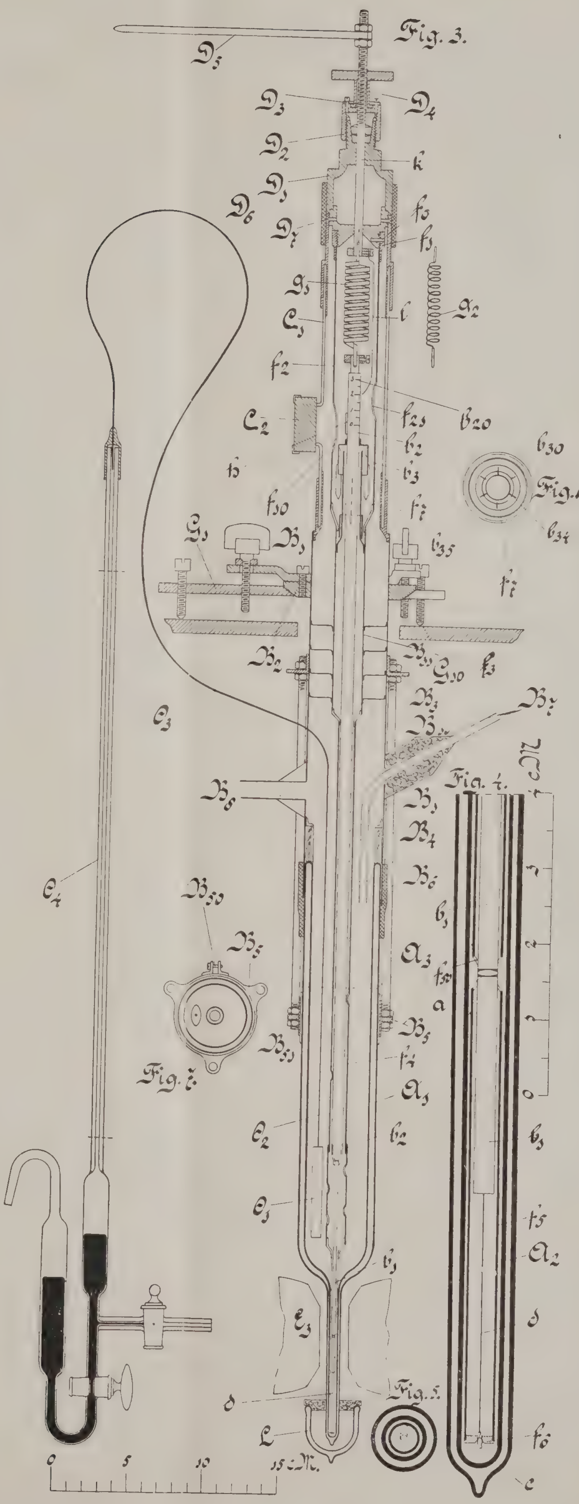


Fig. 2.





Communication No. 114.

PIERRE WEISS and H. KAMERLINGH ONNES. "*Researches on magnetization at very low temperatures*".

§ 1. *Object of the research; results.*

a. Introduction. The extension to all ferromagnetic phenomena of LANGEVIN'S [1]) kinetic theory of magnetism by means of the hypothesis of the molecular field [2]) rendered the testing of deductions from this hypothesis by experimental data of great importance. The first results of this comparison were very encouraging; in some respects a remarkable correspondence was found. For instance the curves calculated for the intensity of the magnetization at saturation as a function of the temperature corresponded very well with those which had been found experimentally for magnetite at temperatures above the ordinary. Moreover, the law determining the susceptibility above the CURIE-*point* [3]) developed from the hypothesis of the molecular field was found, in CURIE'S experiments and in others which will soon be published, to be accurate over a temperature range of some hundreds of degrees. Finally the sudden changes in the specific heat at the CURIE-point were in correspondence with the values calculated from magnetic data. But other observations do not correspond so well with the theory. Fig. 1 Pl. I, in which the theoretical curve for the change of saturation-magnetization with temperature is shown by the full curve *a*, also by the marked points shows the experimental results for magnetite, and the corresponding curve, *b*, for nickel [1]). The last curve is drawn to such a scale that the best possible correspondence with the theoretical is obtained at the CURIE-point. In contrast with what was found for magnetite, nickel shows a deviation from the theoretical gradually increasing over the whole curve. Iron and cobalt behave practically the same as nickel. When all this is taken into consideration it is seen that the hypothesis of the molecular field is of the nature of a working hypothesis; the partial confirmation shows that the hypothesis contains a kernel of truth, and from the experimental deviations one will have to see how it should be modified or extended while still retaining its essential features.

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[1]) LANGEVIN. Ann. Chim. et Phys. 8 Sér. t. 5, p. 70; 1905.

[2]) P. WEISS. Journ. de Physique 4e Sér. t. VI, p. 661; 1907.

[3]) In this Communication we shall give the name CURIE-point to the temperature at which spontaneous ferromagnetism ceases. This is by no means inconsistent with CURIE'S idea that the transformation temperature is a function of the strength of the field, since the temperature at which *spontaneous* ferromagnetism ceases is the temperature obtained by reducing the field to zero.

It is not probable that these modifications will attack the property of reacting against the orientation by the magnetic field that has been ascribed to the kinetic energy, or that they will come into conflict with the manner in which the MAXWELL-BOLTZMANN partition law has been employed. Not only are these hypotheses of fundamental import, but they are still further forced upon our consideration by the ease with which they account for the fact that for paramagnetic substances the susceptibility varies inversely as the absolute temperature — an experimental law that is one of the most firmly established for a number of substances. In their important investigations upon the magnetization of the elements, of which an account was given at the last meeting [2]), H. DU BOIS and HONDA have, it is true, shown that this law of the dependence of susceptibility upon temperature is not generally valid, and that paramagnetism also occurs which is independent of the temperature or increases with increasing temperature. But it is by no means the case that the foregoing hypotheses should be discarded on that account; what we learn from experiment in this case is only that these suppositions are not sufficient to explain magnetism as a whole. In particular it will be necessary to revise LANGEVIN's hypothesis that the magnetic moment of a molecule is constant, or at least quasi-constant, and also that concerning the nature of the mutual action of the molecules, which until now has been represented by the introduction of the molecular field. For an estimation of the value of both of these hypotheses, experiments at low temperatures are especially valuable. For it is only at the absolute zero that the magnetization gives the sum of the molecular magnetic moments, as it is only then that heat-motion can no longer prevent the magnetization from attaining its full value; and at low temperatures, too, is the strongest demonstration of the mutual action of the molecules to be expected, since they are then at the smallest possible distance from each other.

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[1]) According to preliminary measurements. Accurate experiments upon the three metals and magnetite are in progress

[2]) Proc. Kon. Akad van Wet. Jan 1910.

b. Ferromagnetic substances. We have, therefore, aimed at the continuation of the curves connecting magnetization and temperature in the three ferromagnetic substances and in magnetite down to the neighbourhood of the absolute zero. By utilising the methods and appliances [1]) suitable for long-continued accurate measurements at such constant temperatures as are obtainable with liquid hydrogen, we have been able in our measurements to reach a temperature of 20°.3 K. with hydrogen boiling under atmospheric pressure, and of 14°.0 K. with hydrogen near its melting point. The number of degrees on the absolute scale which separate these experimental temperatures from the absolute zero is but such a small fraction of the number between the absolute zero and the CURIE-point (even in the case of nickel this number is still so much as 648 Kelvin degrees) that, considering the nature of the curves, we may regard the saturation-magnetization at the absolute zero as being determined by our experiments. All this, of course, with the proviso that the phenomenon in the region to which extrapolation is carried should give no occasion for adopting another point of view. Since the object of the measurements was a determination of the saturation-magnetization, it seemed suitable to direct the experiments towards obtaining data for magnetization in strong fields, and from these the deduction of the law according to which the magnetization approaches its limiting value. But the method chosen for the magnetic measurements, viz: the determination of the maximum value of the couple exerted by a magnetic field of varying direction upon an ellipsoid of the experimental substance, was, as we shall presently show, less suitable for this determination of the law of approach than for comparisons of the magnetization of the substance in the same field at different temperatures. The data to determine the law of approach were therefore made the subject of a separate investigation [1]). This gave the following values for the difference between the magnetization in a field of 10000 gauss and that in the limiting case:

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[1]) H. KAMERLINGH ONNES, Comm. N⁰. 94*f* (1906).

Iron	0.08 °/₀
Nickel	0.1 „
Cobalt (soft)	1.1 „
Magnetite	0.19 „

For these substances, the cobalt excepted, the approach of magnetization as a function of the strength of the field is hyperbolic, so that in a field of 20000 gauss which we reached in our present experiments the above differences were reduced to half their values. Observations by the ellipsoid method in different fields and at both low and ordinary temperatures have not, indeed, enabled us to test the law of approach, but they show sufficiently well that there is no essential difference between the behaviour in this respect at both temperatures; and that at low temperatures, as could well have been supposed, the magnetic hardness does not assume an excessive value, the molecules hindering each other in assuming a new direction.

Further, by means of comparative measurements, magnetizations at ordinary and at low temperatures in fields of great strength were compared, and it was found that the ratio between the two is pretty well independent of the strength of the field. Thus, leaving the result uncorrected for the dilatation between the two temperatures (see p. 14 note 2), we found for the ratio of the intensity of magnetization at 20°.3 K. and at ordinary temperature the following:

Nickel	(17°.3 C.)	1.0548
Iron	(20° C.)	1.0210
Magnetite	(15°.5 C.)	1.0569.

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[1]) P. WEISS, Arch. des Sc. phys. et nat. février 1910 and Journ. de Phys. 4e Sér. t. IX. mars 1910.

The exact value of the ordinary temperature is given between brackets. In § 5 it will be explained why the experiments with cobalt have not been brought to a conclusion. It is difficult to know exactly the degree of accuracy of these results. Experimental work in every branch was carried out so that an accuracy of 1 in 1000 or even higher could be expected But when one considers the disturbing influences which made themselves felt in the experiments upon cobalt, it seems rather incautious — and this is particularly the case with the magnetite measurements — to ascribe to the results an accuracy greater than 0.5%, even though the occurrences which have brought suspicion upon the cobalt measurements were nearly absent in the case of the other substances, and though in all its properties and particularly in its extraordinarily large magnetic hardness cobalt stands evidently alone. Since our experiments indicate these causes of uncertainty, they show how a higher degree of accuracy may be reached if so desired. The present accuracy is quite sufficient for the treatment of various problems.

The experiments with iron and magnetite were carried to 14°.0 K. The change of magnetization between 20° K. and 14° K. is too small to be expressed in figures. These experiments, therefore, only extend down to 14° K. the temperature region within which the diminution of the kinetic energy and the approach of the molecules to each other do not occasion the appearance of a single new phenomenon.

The portions of the curves for nickel and magnetite which have been newly obtained are given by broken lines in fig. 1, Plate I.

Magnetite is of particular importance on account of the perfect correspondence between observation and theory over the greatest portion of the region between the Curie-point and the absolute zero, and on account of the occurrence of a deviation of observation from theory only at low temperatures. Here, theory gives for the ratio between the magnetizations the value 1.139 instead of the value given above, 1.057. The result that theory and experiment clearly differ at these temperatures is corroborated by earlier experiments upon four samples of different kinds of magnetite, two obtained from natural crystals, the third from a fused natural crystal, and the fourth from artificial magnetite. These gave the following values for the ratio between the magnetizations at the temperature of solid carbon dioxide (— 79° C.) and ordinary temperature:

	1.033	ordinary temperature 16° C.
	1.042	23°.2
	1.043	24°
	1.037	21°.5
mean	1.039	21°.2 C.

while theory gives 1.053 for the same temperature.

An analogy thus seems to exist between this and compression and expansion by heat, for which VAN DER WAALS's theory and law of corresponding states are supported better as a rule in the neighbourhood of the critical point than at low reduced temperatures where the ideal representations of the molecule and of molecular attraction no longer cover the phenomena sufficiently well and the differences between the specific properties of the real molecules appear.

The hypothesis that molecular magnets are essentially invariable would be supported conclusively if there existed simple relations between the magnetic moments as calculated per atom, which one might be led to suspect from the increase by regular steps of the saturation-magnetization of the three metals.

The following table in which the numbers in the first column are taken from the paper [1]) referred to above and in which the relative increase for cobalt is estimated from comparison with iron and nickel shows that this is not the case. The data are not corrected for the dilatation (see p. 14 note 2).

	Specific saturation at temp. ( )	Coefficient of increase by reduction to low temp.	Specific saturation at low temp.	Atomic weight or $^1/_3$ mol. wt.	Moment of gram atom.
Ni	54.6 (17° C.)	1.0548	57.6	58.7	3381
Co	162 (17° C.)	1.01	163.6	59	9650
Fe	217 (20° C.)	1.0201	221.6	56	12410
$FeO^4/_3$	90.75 (15°.8 C.)	1.057	95.9	77.33	7417

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[1]) P. WEISS. Arch. des Sc. phys. et nat. février 1910 and Journ. de Phys. mars 1910.

Errata Communication N⁰. 114.

p 8, p. 24 and p. 30, note 1: for mars read mai.

In connection with this we must not lose sight of the fact that although the proof that the above quantity is of fundamental significance may have escaped us, still there is nothing whatever to justify an opposite conclusion.

When we look upon our measurements as a whole we remain inclined to retain the hypothesis that in ferromagnetic substances the magnetic atom does not in itself change much with temperature. There were indeed reasons for questioning if this approximate invariability, granting that it was proved in other circumstances, still existed at extremely low temperatures. Electrical resistance of metals, phosphorescence of sulphur compounds, absorption of light by the salts of the rare earths with or without magnetic field, all, at very low temperatures, exhibit characteristics that one may try to explain by ascribing them to forces exerted by ponderable matter upon electrons; these forces in that explanation become of primary importance when the temperature sinks to that of liquid hydrogen, and it is ascribed to them in particular, that they make the current-carrying electrons in metals suffer an important diminution in number at very low temperatures, by their being, as it were, frozen to the atom by the low temperature [1]).

It would also be possible that the motions of the electrons which cause magnetism while remaining constant or changing not much at other temperatures, begin to show considerable changes at very low temperatures.

The negative result that nothing happens even at the lowest temperatures, which should throw doubt upon the relative smallness of the variability of the magnetic atom itself, is not perhaps without importance when regarded as a means of weighing the value of the above assumptions regarding the phenomena mentioned, or as a means of separating the group of electrons which occasion magnetism from groups which form the prime factors of other phenomena.

c. Vanadium, chromium, manganese. The question has often been asked if a gap which cannot be bridged over exists between the ferromagnetic metals of the iron group on the one hand and the paramagnetic metals of the same group on the other, or if the latter metals should also exhibit a very low CURIE-point if the temperature were sufficiently lowered.

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[1]) Cf. H. Kamerlingh Onnes, Suppl. N⁰. 9 p. 27 1904 and P. Lenard, H. Kamerlingh Onnes and W. E. Pauli, Comm. N⁰. 111, p. 3, note 2 1909.

CH. ED GUILLAUME[1]) says with reference to the HEUSLER alloys of Mn, Al, Cu and Mn, Sn, Cu which are ferromagnetic: "The reason for this can be found in the fact that aluminium or tin when compounded with manganese, a metal from the magnetic group, raises its transformation temperatures, which, following an hypothesis already suggested by FARADAY, ought to lie very low". It can indeed be seen that aluminium and tin raise the melting points of various alloys which they form with other metals (the series Al—Au, Al—Sb, Na—Sn) and seem to possess the general property of raising temperatures of transformation.

We might, therefore, expect that vanadium, chromium and manganese should at very low temperatures exhibit either the characteristics of ferromagnetism (magnetization not proportional to strength of field, saturation, hysteresis) or, in conformity with CURIE's law, a strongly increased paramagnetism. The susceptibility at the temperature of solid hydrogen should be about twenty times as great as at ordinary temperature[2]). At this time we were not yet aware of the results published last month by H. DU BOIS and HONDA[3]), from which it appears that the inverse proportionality of paramagnetism to the absolute temperature is but one of the possible cases. To get an idea of the order of magnitude of the expected phenomena we may suppose that the paramagnetic γ iron still exists at 14° K. with the same CURIE constant (product of absolute temperature by susceptibility). In that case a value of about 400 is found for the magnetization of this substance in a field of 20000 Gauss.

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[1]) CH. ED. GUILLAUME. Actes de la Soc. helv. des Sc. nat. Vol. I p. 88, 1907.

[2]) A similar supposition formed the starting point of a research by H. KAMERLINGH ONNES and A. PERRIER, closely connected with the present subject. This investigation was undertaken at the same time as the present research and will shortly be published. Using the method of the maximum couple and the hydrostatic rise the magnetizations of liquid oxygen at various temperatures and of solid oxygen at the temperatures of boiling and solidifying hydrogen were measured. The increase of the magnetization at low temperatures was found to be very great, though not so much as was expected, and a distinct deviation from CURIE's law and a characteristic curve were found.

[3]) H. DU BOIS and HONDA l. cit.

Some time ago GEBHARDT[1]) determined the susceptibility of manganese at ordinary temperature and found $K = 322.10^{-6}$ (density 6.4). The above calculation gives a value 134 for the magnetization of this substance in the same circumstances. And as the deflection in our apparatus is proportional to the square of the magnetization one would obtain a deflection 18 times smaller in the case of γ iron or 160 times smaller in the case of manganese than that which was found for iron at the ordinary temperature; as this was 100 cm. the manganese deflection should still be quite easily readable.

When we now introduced into our apparatus roughly formed ellipsoids of MOISSAN vanadium and GOLDSCHMIDT chromium and manganese in succession, the awaited change did not appear. In every case the deflection at the temperature of solid hydrogen as well as at that of hydrogen boiling under atmospheric pressure remained the same as it was at ordinary temperature, that is, to a few tenths of a millimetre, and these must be ascribed to the magnetism of the suspending apparatus. There was therefore no ferromagnetism and we were obliged to choose between the following two hypotheses for these substances. We were either dealing with paramagnetism of a new kind or with diamagnetism, which is also found in copper while most of the salts of this metal are paramagnetic. DU BOIS and HONDA'S paper in which these three metals are classified under those whose paramagnetism is invariable or increases with the temperature shows that the first assumption is the correct one. The behaviour of copper made us consider the other hypothesis a reasonable one.

One could always assume that the paramagnetism, which, as a general rule is ascribed to the metallic manganese, results from the presence of its oxides, which are strongly magnetic, or of a small quantity of iron. To put this assumption to the proof we prepared very pure manganese from MERCK'S pure chloride, which had been proved free from iron. The preparation was accomplished by electrolysing the salt between a cathode of distilled mercury and an anode of platinum alloyed with 40% of rhodium which is not attacked by the chloridion. The amalgam obtained in this way was separated in a stream of pure, dry hydrogen. In this way a grey powder was obtained which when compressed in a glass tube as a mould took the shape of a solid rod. A rod prepared in this manner exhibited paramagnetism. A glass tube with the powdered manganese was also paramagnetic. The same manganese contained in a magnesia boat was thereupon fused in an electric resistance furnace and in an atmosphere of hydrogen. In this way an ingot was obtained which was covered with a light oxidised crust. It was found impossible to grind away this crust with quartzpowder, since the metal was of the same hardness as quartz. Emery could not be used as it is magnetic. The impure crust was therefore turned off with a diamond tool, and a small cylinder of pure substance was obtained.

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[1]) GEBHARDT, Inaug. Dissert. Marburg 1909.

This cylinder was found to be *ferromagnetic*. Fig. 2 Pl. I gives the hysteresis curve for this substance. The maximum value of the specific magnetization is 100 times weaker than that of iron, and the coercive field is 670 gauss, that is to say, 10 times as strong as the coercive field of steel which is used for the preparation of good permanent magnets. This peculiar substance seems moreover to have striking magneto-crystalline properties. The rod was strongly attracted between the poles of a magnet and placed itself perpendicular to the field.

Manganese of the same degree of purity can therefore occur in two states: paramagnetic and ferromagnetic. GEBHARDT's experiments give a susceptibility five times greater than that observed by DU BOIS. If GEBHARDT's powder was not impure or oxidised, it is thus possible that there are two paramagnetic states.

As regards the ferromagnetism of manganese, this had already been observed by SECKELSON [1]) with electrolytic manganese that was liberated at 100° C. from the chloride upon a platinum wire, and with a regulus prepared by BUNSEN from manganese fluoride. The very indefinite observations concerning the magnetization which he published do not contradict with our measurements.

By a more direct method we have proved the absence of strong magnetism in vanadium, chromium and manganese at low temperatures. For this purpose we introduced ellipsoids of the three substances into a narrow unsilvered vacuum tube whose walls were separated by the smallest possible distance; this was placed in a second similar tube also as narrow as possible and filled with liquid air. We then determined at which distance the ellipsoids were attracted from the bottom of the tube to the poles of the magnet. This experiment was made first with the inner tube empty, and then with the inner tube filled with liquid hydrogen. The following results were obtained:

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[1]) SECKELSON, Wied. Ann. LXVII, p. 37, 1899.

	Ordinary temperature.	In liquid hydrogen
Vanadium	Not attracted	The same as at ordinary temperature
Manganese	Attracted from distance of 6 to 8 mm.	
Chromium *a*	„ „ „ „ 12 „	
Chromium *b*	„ „ „ „ 60 „	

The results for Chromium *b* which probably contained a small splinter of iron must be rejected. We also found further that a crystal of iron sulphate at ordinary temperature was attracted from a distance of 25 mm. while in liquid hydrogen it was attracted almost from the base of the magnet. Thus the weak magnetization of the three metals was found to be practically invariable, while the iron sulphate exhibited a very great increase in magnetic properties.

This experiment is well adapted for displaying the characteristic difference between the two groups of substances and is a typical example of the significance which even the simplest experiments acquire within the fallow region of very low temperatures.

§ 2. *Methods and apparatus.*

a. Discussion of the method of the maximum couple. We measured the intensity of magnetization by measuring the couple exerted on a prolate ellipsoid of revolution of the experimental substance arranged so that the angle of the field with the major axis of the ellipsoid might be varied. The expression for the couple is

$$M = (N_1 - N_2)\ I^2 v \sin \Phi \cos \Phi$$

where N_1 and N_2 are the coefficients of demagnetization of the ellipsoid, I the intensity of magnetization of the substance, v the volume, and φ the angle between I and the major axis of the ellipsoid. The maximum value of this couple is

$$M = \frac{N_1 - N_2}{2} \cdot I^2 v$$

for $\varphi = 45°$. Hence to measure I it is not necessary to know either the strength or azimuth of the field which yields the maximum couple. To make use of these methods the ellipsoid is suspended from a torsion-spring whose displacement is determined by a mirror-method, and an electromagnet turning round a vertical axis is used. The method has already been described [1]). Its advantages consist of the small range over which strong fields are necessary and the extreme simplicity of the relative measurements [2]). We shall now discuss two sources of error which affect it and which, although they may be made as small as one wishes in theory, render it less suitable for the search after the law of approach to saturation, although they do not take away from its value as a method of comparing in the same field two successive and slightly differing states of the same substance.

Influence of non-uniformity of the field.

The ellipsoid is placed in the centre of a magnetic field possessing the symmetry of a body of revolution. The strength of the field at this centre is a maximum for a displacement in the plane of the equator, y, and a minimum for a displacement in the direction of the x axis. It is given by the series

$$H = H_0 + \frac{x^2}{1\,.\,2}\left(\frac{\partial^2 H}{\partial x^2}\right)_0 + \frac{y^2}{1\,.\,2}\left(\frac{\partial^2 H}{\partial y^2}\right) + \ldots.,$$

which, remembering the equation $\triangle V = 0$ for the magnetic potential V, and converting to polar coordinates r and θ, transforms into

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[1]) P. WEISS, Journ. de Phys 4 sér. t. VI, p. 655, 1907.

[2]) For comparing the intensities of magnetization I and I' at two temperatures we have to take into account that $v = m/d$, m being the mass of the ellipsoid and d its density, so that $\frac{I}{I'} = \frac{\sqrt{M}}{\sqrt{M'}} \cdot \frac{\sqrt{d}}{\sqrt{d'}}$ and $\frac{\sigma}{\sigma'} = \frac{\sqrt{M}}{\sqrt{M'}} \cdot \frac{\sqrt{d'}}{\sqrt{d}}$.

The dilatation at the low temperatures and therefore the ratio of d to d' being unknown, we have omitted the correction for the difference between this ratio and unity, the value of which may be estimated at 0.004.

p. 15 line 13 from the top: for nothwithstanding read notwithstanding.

$$H = H_0 + \frac{r^2}{2}\left(\frac{\partial^2 H}{\partial x^2}\right)_0 \left(\cos^2\theta - \frac{1}{2}\sin^2\theta\right).$$

Now, the energy of a volume-element dv of the ellipsoid which we consider to be very long in comparison with the transverse diameter and magnetized with uniform intensity I in the direction of the field, is

$$W = - IHdv$$

and therefore the moment of the couple exerted by the field on this element is

$$dM' = \frac{\partial W}{\partial \theta} = \frac{3}{2}\, dv \;.\; I\left(\frac{\partial^2 H}{\partial x^2}\right)_0 r^2 \sin\theta\cos\theta.$$

The couple exerted by the field H_0 on the ellipsoid is

$$M = (N_1 - N_2)\, I^2 v \sin\Phi \cos\Phi.$$

In very strong fields the condition is fulfilled that the magnezation is parallel to the external field nothwithstanding the demagnetizing forces of the ellipsoid, and therefore $\theta = \Phi$.

Hence the disturbing moment dM' varies with azimuth of the substance in exactly the same manner as the chief couple M. The maximum value of the couple dM' is

$$dM' = \frac{3}{2}\, dv\, I \,.\left(\frac{\partial^2 H}{\partial x^2}\right)_0 r^2,$$

which for the whole ellipsoid gives

$$M' = \frac{3}{10} I \left(\frac{\partial^2 H}{\partial x^2}\right)_0 v \,.\, a^2,$$

where a is the semi-major-axis of the ellipsoid.

Let us now make the assumption that the field changes conformally, and let us call the field 1 cm. from the axis in the direction of the y-axis $(1 - \varepsilon)\, H_0$, then

$$\varepsilon H_0 = \frac{1}{4}\left(\frac{\partial^2 H}{\partial x^2}\right)_0,$$

and therefore

$$M' = \frac{6}{5} I \varepsilon\, H_0\, v \,.\, a^2,$$

and the ratio between the maximum values of the couples is

$$\frac{M'}{M} = \frac{6}{5}\,\varepsilon\, a^2\, \frac{H_0}{(N_1 - N_2)\, I}.$$

With constant magnetization, therefore, the second last equation shows that the disturbing couple increases proportionally to the strength of the field. In the *I-H* diagram, a sloping instead of a horizontal asymptote will be found. This was shown clearly in some former experiments. If the field is constant the disturbing couple increases with I. Therefore, if in the measurements with the greatest values of I for which the experiments are carried out, made with a certain apparatus, the disturbing couple does not make its presence felt, then *a fortiori* is it negligible for the smaller values of I. The last equation shows that the *relative* value of the couple for non-uniformity of the field increases as the intensity diminishes. Hence it is to be feared particularly when one works with small magnetizations, and when, to increase the sensitivity of the apparatus, the torsion spring is replaced by a weaker one.

For the purposes of our measurements it is sufficient to get an idea of the order of magnitude of the error. For this purpose the non-uniformity of the field was measured for three different values of y; it was found to be proportional to y^2 with $\varepsilon = 0.0087$ as factor. With $a = 0.15$ it follows that $\frac{M'}{M} = 0.00023 \frac{H_0}{(N_1 - N_2)\,I}$. For the ellipsoids used $N_1 = 1.90$ and $N_2 = 5.59$, and $(N_1 - N_2)\,I$ is almost 6600 gauss for iron and 1800 gauss for nickel. Hence, for iron the correction would be scarcely 1 in 1000, while for nickel it would increase to some thousandths.

Reaction of the ellipsoid on the pole-pieces.

When the ends of the ellipsoid come into the immediate neighbourhood of the end surfaces of the poles, they exert a noticeable influence upon the distribution of magnetism in the pole-pieces, and the couple becomes increased thereby. This fact was established by previous experiments with a larger electromagnet with flat pole-pieces of 15 cm. diameter. In these experiments was measured the couple exerted upon an ellipsoid with various distances between the poles by a field of the constant value of 9770 gauss regulated each time by passing the required current. In this way the following values were obtained for an iron ellipsoid 9 mm. long and 4 mm. thick

Distance between poles	Maximum couple
9 mm.	335.6
15 „	320.45
23 „	319.32
35 „	319.18
47 „	319.08

The law according to which this magnitude changes shows that the change is not a consequence of the non-uniformity of the field; for just when the disturbance reaches its greatest value, the field is most regular owing to the closer approach of the flat pole-pieces. For distances of 23 mm. and greater the influence is insignificant, and the couple is constant.

b. Electromagnet. From what has been said about the influence of the ellipsoid and the pole-surfaces it follows that the distance between the poles should be about three times the length of the ellipsoid. The total thickness of the four walls of the DEWAR tubes and of the holder (§ 2*c*) could not be made smaller than 5 mm. Hence, keeping account of the difficulty on the one hand of obtaining strong fields of wide extension and on the other hand of reducing very small ellipsoids to the correct form, we decided upon an interpole distance of 9 mm. and a length of 3 mm. for the ellipsoids.

With this distance comparatively strong fields (up to 25000 gauss) may be excited with a magnet whose cores are 9 cm. in diameter. The electromagnet of this power which was used in these experiments has already served for magnetic experiments at high temperatures. It has already been described [1]) and is represented diagrammatically in fig. 1 Pl. II. Comparatively light (132 KG.) and, taking its power into account, easily transported, it was possible to study it in Zürich and to use it in Leiden. Two hand-wheels, the position of each of which is read from a divided circle, communicate a horizontal micrometric movement to the pole-pieces.

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[1]) G. ZINDEL. Revue électrique 20 Juin 1909 and Elektrot. Zeitschr. XXX, p. 446, 1909.

The magnet turns upon a vertical axis and for that purpose is mounted upon a ball-bearing support. The azimuth is determined by means of a fixed mark on a cylindrical scale E_2 attached to the movable portion of the supporting base. Each of the coils has 1500 turns of 2.5 mm. wire and has a resistance of about 2 ohms. As the coils are arranged for a current of 10 amp. under ordinary circumstances, and as the current can for a short time be increased to 25 amp. the number of ampère-turns at ones disposal may reach as high as 75000. The water circulation E_5 between the double walls of the coils has this immediate advantage that the duration of an experiment may be doubled, but it is chiefly of importance in protecting the pole-pieces from heat. Such a heating would lead to various difficulties, of which one of the worst would be that the strength of the field would noticeably change, for the expansion of the comparatively long core by heat could distinctly alter the comparatively short distance between the poles.

c. *Cryogenic apparatus.* As it was necessary to shut off from the air the space in which the ellipsoid was freely suspended since it contained liquid hydrogen and its vapour, a fairly complicated cryogenic apparatus had to be employed. This is shown diagrammatically in Pl. II fig. 1 and in section in fig. 3. The apparatus consists chiefly of three tube-shaped portions which, naming from outside inwards, we call the *cover*, the *adjusting tube* f, and the *holder* b. The cover consists of a silvered vacuum tube A, a brass tube B, a glass tube C, and a cap D which shuts off the apparatus from the air.

Holder. The ellipsoid a (figs. 3 and 4) can turn round a vertical axis with the holder b in which it is fixed. For the greater part of its length the holder is made from a tube b_2 of german silver — a substance that is rigid, little magnetic, and a bad heat-conductor The lower end is joined to a copper rod b_1, which has only a very weak inherent magnetism. The holder is connected to the rod k by the spiral spring g_1 (g_1 was used for iron and cobalt; the weaker spring g_2 which was used for nickel and magnetite is shown at the side). To make the equilibrium stable and to prevent the ellipsoid from being attracted to the poles of the magnet the holder is held fast underneath by a wire of platinum-iridium of 0.1 mm. diameter, for the torsion of which a correction need hardly be applied (§ 4).

The tube b_2 and the rod b_1 are carefully adjusted on the lathe and the ellipsoid a (fig 4) is fixed carefully in a cylindrical opening the diameter of which is equal to the minor axis of the ellipsoid. If the ellipsoid is nickel or magnetite it can be fixed in position with a little wax. With iron and cobalt, however, the ellipsoid is subject to such strong forces that it is necessary to clamp it fast by covering it with a thin piece of sheet copper and then driving it forcibly into the opening. The turning of the ellipsoid is transmitted through the rod b_1, and the thin-walled german-silver tube [1]) b_2 [2]) to the mirror h. From the mirror through the opening f_{10} and the window C_2 (figs. 1 and 3) the torsion of the spring g_1 is read. A glass scale 1.5 meters long, and subdivided into half millimeters is used; it is placed at a distance of 4.325 m. and is illuminated by spherical mirror strips [3]). The tension of the spring is regulated by the rod k (fig. 3), which passes through a stuffing box D_2 in the cap D. Vertical motion is communicated to k by turning the nut D_4 and at the same time preventing the motion of D_5. The tension is read through the opening f_{21} from the pointer l on the scale b_{20}. Before mounting the apparatus, that division of the scale b_{20} is determined which corresponds with the tension that is to be used, by suspending known weights from the stretching wire.

The apparatus is, like a stretched string, very liable to start vibrating under the influence of small impulses. This tendency is counteracted by immersing the vanes of a damper b_3 (fig. 6 and fig. 3) in oil contained in a circular vessel divided into different chambers by the partitions b_{34}. These partitions are attached to a cylinder which turns with slight friction in the adjusting tube and is therefore carried round by the vanes b_{30} whenever the holder must experience a somewhat greater torsion (§ 4) ¹). The vanes must be wholly immersed in the oil so as to ensure that capillary reactions do not bring forces into play (see § 4), whose torsional effect could not be neglected. In strong fields the torsion oscillations are damped extremely well by the FOUCAULT currents.

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[1]) A slight twisting of this tube is of no account. Only that portion of the apparatus between the mirror and the cap acts as a spring. Twisting of the portion of the apparatus below the mirror only transmits the couple to that spring, its sole effect is to slightly, but not noticeably, alter the azimuth of the magnet.

[2]) In the diagram, Pl. I fig. 3, the indicating line at b_2 stops short by mistake at the adjusting tube f_4.

[3]) H. Kamerlingh Onnes, Comm. N°. 25. (1896).

The whole holder and spring hang in the adjusting tube f the upper end of which is screwed to the cap D; this cap also carries the rod k, and is itself supported by the glass tube C. The adjusting tube, consisting of the portions f_2, f_3, f_4, f_5, is three times diminished in cross-section. The lowest portion f_5 is narrow and surrounds the rod b_1 of the holder as closely as possible. Against the bottom f_6 (fig. 4) rests the cone c, which is soldered to the wire d and serves to keep it taught. A slit in the bottom allows the conical portion to be placed in position (fig. 5). When the apparatus is put together the adjusting tube sinks into the DEWAR vessel A so that the thin tube f_5 is centred in the narrow portion of the vacuum tube. The adjusting tube as well as the tube f_4 of the holder is made of german-silver.

To mount the adjusting tube already containing the holder in the cover, the cap D is screwed to a bronze ring cemented to the glass tube C of the cover; the screws D_7 are tightened, and the junction is made air-tight by means of the rubber sleeve D_6 which is smeared with rubber solution and bound with copper wire. The lower end of the glass tube C is cemented to a second bronze ring, which is soldered to the brass tube B of the cover. To the centre of this brass tube is attached a ring B_3 carrying the bolts of the supporting rods B_4 which hold the vacuum glass in position.

The DEWAR tube itself consists of a narrow lower portion A_2 completely silvered and a wider upper portion that is silvered op to A_3 (the upper portion is left transparent so that we might be sure that we were not allowing too much liquid hydrogen

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¹) It is essential to free the oil beforehand from volatile substances, and also to prevent the accumulation of air bubbles under the oil, since the apparatus has to be completely evacuated after it is put together.

p. 20 line 5 from the bottom: for op read up.

to enter the glass). It fits into the brass tube B_1 and is protected by a wooden ring. The supporting rods B_4 keep the vacuum tube in position and at such a height that it is just clear of the wooden safety ring. Fig. 7 shows how, by means of the screw B_{50}, the vacuum glass protected by a layer of paper is clamped to the thin brass ring B_5 to which are attached the ends of the supporting rods B_4. The lower portion of the vacuum tube has an external diameter of 8 mm. and an internal diameter of 5 mm. The glass walls are 0.5 mm. thick, which leaves only 0.5 mm. as the distance between the two silvered walls.

The apparatus is centred by placing it on an auxiliary support by means of the ring B_2. Before the vacuum tube is yet in position, the narrow portion f_5 of the adjusting tube is adjusted by a central ring in an adjustable centring-plate. The loose ring is then removed from the plate and a second is fitted such that it just fits the narrow portion of the lower end of the vacuum tube. The nuts B_{31} serve to bring the vacuum glass to its proper position, and, as before, it is made air-tight by a rubber sleeve B_6, which is smeared with rubber solution and bound with copper wire. By adopting this method of attaching the vacuum tube one need not fear alteration of the cover when the apparatus is evacuated, and only small further adjustments are necessary for recentring the apparatus after evacuation.

In the tube B is soldered the steel capillary Θ_3 (figs. 1 and 3) of a helium thermometer [1]) with german silver reservoir Θ_1 (figs. 3 and 7) and glass stem Θ_4, which is permanently attached to this portion of the cover. The quantity of helium is so chosen that at the boiling point of oxygen the mercury stands at a mark in the lower portion of the stem, and at the melting point of hydrogen at one in the upper portion. If, as is the case with hydrogen boiling under ordinary atmospheric pressure, the temperature is sufficiently well known without reading the thermometer, the thermometer is still necessary, however, to indicate the position of the upper surface of the liquid gas which is no longer visible beneath A_3. As soon as the level sinks below the upper end of the reservoir Θ_1 of the thermometer, the mercury in the stem Θ_4 sinks.

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[1]) Compare the apparatus for the liquefaction of helium. H. KAMERLINGH ONNES Comm. N°. 108, 1908.

d. First the electromagnet is adjusted which operation is independent of the centring of the adjusting tube, the holder and the vacuum tube. The axis round which it turns is made vertical, and then the pole distance is centred round this axis. Next the centre of the truncated spherical socket G_{10} (figs. 1, 2 and 3) is made coincide with the axis round which the magnet turns. It is supported by a plate which is attached by two beams to the freestone pillar $\mathfrak{G}$. The cryogenic apparatus is then brought from its auxiliary support and arranged in its proper position by placing the ball-shaped portion of the surface of the ring B_2 in the concentric socket G_{10}; the centring of the narrow portion of the vacuum tube on the turning-axis of the magnet is completed by means of wing nuts on the ring B_2. This centring must be done with great accuracy, for the magnet must turn freely and the distance between the vacuum tube and either pole is not more than half a millimeter. It can, however, easily be accomplished to 0.25 mm.

e. Liquid hydrogen is introduced into the apparatus by a german silver tube B_7 (cf. Comm. N^0. 94*f*). The gas formed by evaporation escapes through B_8 (figs. 3 and 1) and through the valves K_1, K_2 (fig. 1) to a gasometer or to a vacuum pump. By means of the valves the vapour pressure is regulated, and its value is read on a manometer H which at the same time acts as a safety valve. In experiments made in the neighbourhood of the melting point of hydrogen the pressure was kept slightly above that of the triple point.

Before introducing liquid hydrogen through the tube B_7, which is closed by a rubber tube with a glass stopper, the air is pumped out of the apparatus through the valve K_2. It is absolutely essential that the apparatus should be air tight, for traces of air would solidify in the liquid hydrogen and, owing to magnetic attraction, would collect in the neighbourhood of the ellipsoid.

To prevent the cooling of the upper portion of the apparatus containing the torsion spring by the boiling hydrogen, a number of large openings are made in the tube f_4 (fig. 3) arranged in such a way that no injury is done to its resistance to torsion. In addition to this copper screens surrounding f_3 and soldered to

B_1, are arranged so that the tube moves with slight friction in them. A little cottonwool placed on the bottom of the vacuumglass and attached to the holder lessens the sudden bubbling[1]) up of the hydrogen.

Further additions of liquid hydrogen are made in the same way as the first. As a rule various series of measurements could be made with a single filling with hydrogen. The point of the vacuumglass which could not be silvered was protected by a small silvered vacuum beaker L containing liquid air. When the portion of the apparatus above the diaphragms B_{10} is again at ordinary temperature after a filling with liquid hydrogen, one can hardly notice that there is liquid hydrogen in the apparatus at all, if it is not above A_3.

In the course of time a little mist is precipitated on the vacuum tube. By surrounding the tube at A_1 with blotting paper, the moisture is prevented from trickling down between the pole-pieces. Furthermore a stream of air is directed against the tube between the pole-pieces. Hence the pole-pieces are in no way affected by the cryogenic operations.

f. The springs are phosphorbronze. This substance is non-magnetic and acquires very little permanent set. Springs of the same constant can be made by winding a spiral either of a thin short wire or of a much longer thicker one. Of the two, the one which has the greater mass will experience the smaller specific changes, and consequently will be the more perfectly elastic in working. This circumstance has been duly taken into account. The springs are provided with straight extensions in the direction of their axis and are connected with the holder and the rod k (fig. 3) by screws. The turns of the spirals do not touch each other. The temperature of the spring is measured by a mercury thermometer that is clamped against the cap D and with it is insulated with wool. The constants of the two springs used are 261000 and 22300 dyne-centimeters per radian. The corrections for the influence of the stretching wire and for the temperature change of the spring will be discussed in § 4.

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[1]) Should this occur one must ensure that the oil of the damper is not cooled by the drops that are thrown up.

The ellipsoids of iron, nickel and cobalt are 3 mm. long and 1.333 mm. thick. They have been made with great accuracy by the Société Genevoise pour la Construction d'Instruments de Physique. They were turned under a microscope giving a 30-fold magnification and provided with a camera lucida so that the image of the object and an enlarged drawing could be superposed. Measurements with the dividing engine have shown that the ellipsoids are very accurately shaped.

The iron was obtained by melting pure electrolytic MERCK iron contained in a magnesia boat in an electrical resistance furnace and in an atmosphere of nitrogen. The nickel and cobalt were prepared in the same way, starting with the purest possible nickel and cobalt powder specially prepared by MERCK for these experiments. The magnetite was obtained by constructing an approximate ellipsoid from a drop of very pure magnetite obtained by melting pure MERCK sesquioxide in an oxy-hydrogen flame. Since experiment showed that it was only at very high temperatures that the last trace of oxygen was driven out and real magnetite [1]) obtained an iridium cupola was used for this operation.

Ellipsoids of appoximate shape were also constructed from GOLDSCHMIDT chromium and manganese and MOISSAN vanadium. As can easily be seen it is not necessary for comparative experiments that the ellipsoids should be constructed with particular accuracy. This was, moreover, experimentally demonstrated for magnetite, of which various samples roughly worked to various ellipsoidal shapes were used for obtaining curves for the thermal change at high temperatures, and these curves were in agreement with the theoretical curve, and consequently with each other.

§ 3. *Experimental method.* As mentioned in the introduction our aim was not to obtain absolute values for magnetization in strong fields at ordinary temperature and at the temperature of liquid hydrogen, but to compare the values at these temperatures; for we might expect that the change would be only a small fraction of the quantity to be measured. Hence it was an obvious procedure to make observations at these temperatures alternately in the same field. The change, however, from the one temperature to the other necessitated operations of such duration as to prohibit the use of this method. Hence we usually began with a series of measurements at ordinary temperature, in which the field was made the required series of strengths. Then an analogous series of measurements was made at a low temperature, and after the apparatus had returned to ordinary temperature, some individual measurements were repeated so as to make sure that the apparatus had not in the meantime undergone any change.

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[1]) See also P. WEISS. Arch des Sc. Phys. et nat. févr. 1910 and Journ. de physique, 4e Sér. t. IX mars 1910.

Each series of measurements consists in turn of two branches. First by tentative approximation from both sides for all values of the field those values of the azimuth of the electromagnet are found for which the couple is a maximum. In this way two azimuths are found which are symmetrical with respect to the major axis of the ellipsoid and which exert couples of opposite sign. This determination can be made accurately to within 0.5° to 1°, which is quite sufficient Then follows the true measurement in which the magnet without current is placed in one of these positions, the circuit is closed and immediately afterwards the deflection is read. As soon as this is done, the circuit is broken, the magnet is placed in the symmetrical position; once more the current is allowed to flow and the new deflection is obtained. Since these operations occupy only a short time, the after effects in the spring are of no account. The difference between the scale readings gives twice the value of the couple to be measured, independent of the residual magnetism remaining after the current was broken, which however occasioned only an extremely small couple. The field was given as a function of the current indicated by the ammeter. For these observations the same ammeter (SIEMENS and HALSKE instrument, no temperature coefficient) was used which was employed in the study of the field. This method of evaluating the field was quite sufficient for our purpose. The distance between the pole-pieces was read off the divided cylinders of the magnet and was verified by passing between them callipers which had been previously adjusted to the desired distance. The fields given are corrected for the demagnetizing fields of the ellipsoids.

§ 4. *Corrections and controls; auxiliary measurements.* The inherent magnetism of the holder is not so weak that the corrections necessary for it may be neglected. On that account a series of measurements was made with no ellipsoid in the holder at ordinary and at liquid hydrogen temperatures. With the weaker spring we found:

TABLE I.

Correction for the magnetism of the holder.

	ordinary temperature	$t = 20^\circ.3$ K.
4000 gauss	0.18 cm.	0.26
8000	0.29	0.48
12000	0.36	0.61
16000	0.43	0.73
20000	0.50	0.86
24000	0.57	0.98

For the stronger spring these corrections are multiplied by $\frac{22300}{261000}$; they are very small. Direct measurements have shown that the values calculated in this way are correct, which indicates that the inherent magnetism of the holder is not changed by the various operations of mounting.

There is still a correction to be applied to the couple-ratio for change in elasticity of the steadying wire under the holder when its temperature changes from ordinary to that of liquid hydrogen. To obtain that correction the ratio of the torsion couple of the platinum iridium wire and that of the weaker of the phosphorbronze springs was measured at the two temperatures. This was done in an apparatus similar to the one we have described with the exception that the cap *D* could turn relatively to the cover. By a mirror method the position of the cap was read on a scale at a distance of 175.9 cm. The cap was turned through an angle of about 360°, and the exact measurement of the angle was obtained from the same scale. This angle is the sum of the torsions of the spring and the wire caused by the same couple. The torsion of the wire was read from the mirror of the holder. In this way the ratio of the constant of the wire to that of the spring was found to be

0.0125 at ordinary temperature
0.0144 in liquid hydrogen.

The fourth decimal is uncertain; hence the correction is two thousandths for the weak spring and two ten-thousandths for the stronger. The temperature coefficient of the phosphorbronze spring was obtained from determinations of the period of oscillation of the same oscillating system while the spring was first at the ordinary temperature and then surrounded with steam. By means of the temperature coefficient thus determined viz.:

$$k = -0.00053$$

the observations are reduced to the same temperature.

The temperature of the liquid bath in the vacuum tube was proved to be constant to 0.1 degree, by carrying out temperature measurements with a platinum resistance thermometer placed at different heights in a similar vessel. When placed alongside the thermometer Θ it indicated temperatures in agreement with those deduced from the vapour pressures.

Capillary action in the oil damper.

Care was taken to fill the oil vessel to such a height that the cylindrical ring carrying the vanes of the damper was immersed in the oil so that the vanes should experience no capillary action. But still we wished to know the order of magnitude of the forces brought into play by capillary disturbances; for this purpose we greatly magnified them. A damper as like ours as possible was filled only to such a height that the vanes and partitions intersected the surface of the liquid. The movable portion was suspended by a platinum-iridium wire 20 cm. long and 0.1 mm. thick; deflections were read from a mirror on a scale 2 metres away. The oil vessel was placed successively in two different azimuths such that the approach of the vanes towards the partitions would bring into play couples of opposite moments. The scale deflection was 5 cm. The moment of the couple is therefore of the order of two thousandths of that of the couple exerted on the nickel ellipsoid.

§ 5. *Details of the observations.*

Nickel.

The first series of measurements was made at 17°.2 C.

TABLE II.

H (gauss)	I^2 (cm. of the scale)
2230	89.42
6250	89.97
10270	90.12
13280	90.34
17760	90.50
20300	90.66
21540	90.79
22760	90.81

The scale reading was always corrected for the ratio of the tangent of the double angle to the double angle of the deflection. The zero as determined by the mean of readings to left and right remained constant to a few tenths of a millimetre.

After this series the apparatus was accidentally damaged; it had therefore to be taken to pieces and remounted That occasioned a small change in the magnitude of the deflections. Since the change of I^2 with H is determined by the foregoing series, only two points were subsequently determined at ordinary temperature before and after determinations in liquid hydrogen.

TABLE III.

$t = 19°.5$ C.		Hydrogen at atm. pressure (20°.3 K.)	
H (gauss)	I^2 (cm. of the scale)	H (gauss)	I^2 (cm. of the scale)
before		1780	93.57
16100	91.74	5410	100.49
20540	92.09	8050	101.54

after		11830	101.84
16100	91.79	16100	102.13
20540	92.20	19050	102.34
		20540	102.51
		22020	102.48
		22840	102.49

The zero determined from the mean of readings to right and left changed by about 2 mm.

For $H = 16100$ gauss $\frac{I_{20^\circ.3\mathrm{K}}}{I_{19^\circ.5\mathrm{C}}} = 1.0549$

„ $H = 20540$ „ „ 1.0547

mean 1.0548 not corrected for dilatation.

Cobalt.

The measurements with cobalt dit not lead to the desired result. It was the extreme difficulty of bringing the magnetization of cobalt to saturation encountered in preliminary experiments that had led to the choice of an apparatus of such small dimensions. For the other substances a weaker field would have sufficed, and hence a greater distance between the poles would have served.

In the observations at ordinary temperature something unexpected already happened. Although the mean of the readings to right and left ought to have given the zero-point of the apparatus, the point was actually observed to vary with the field. This change was afterwards seen to be about twice as great at low temperatures. The following figures bring this out clearly. (In the cobalt measurements the external field is given uncorrected for the demagnetizing field of the ellipsoid. When saturation is reached this is about 5000 gauss).

TABLE IV.

Cobalt I at ordinary temperature.

H_e (gauss)	I^2 (cm. of the scale)	calculated zero	
4025	17.16	76.73	
8050	38.14	77.47	the observed
12075	50.48	78.96	zero was
19560	53.24	78.37	not
23340	53.29	78.18	recorded
25650	53.30	78.63	

Cobalt I at temperature of solidifying hydrogen (14°.0 K.)

4025	13.5	77.62	
8050	32.59	78.84	
15820	53.23	81.93	observed zero
19560	54.33	81.40	78.26
21800	54.43	81.16	
23340	54.45	81.02	
24760	54.46	80.08	

From this it appears that asymmetric disturbing forces affect the main phenomenon. It is probable that we are here dealing with phenomena of crystal magnetism arising from the fact that in the small ellipsoid the crystalline elements of the cobalt are not sufficiently numerous to realize isotropy by compensation. The magnitude and sign of these subsidiary actions are independent of the main phenomenon, and they can even be of opposite effect for both azimuths of the electromagnet; they can become of very great importance if the substance possesses a more or less pronounced magnetic plane, and the example of pyrrhotine shows us that their influence becomes greater at lower temperatures. Further, the law of approach to saturation in cobalt which differs from that which holds for the other substances is consistent with the existence of strongly developed magneto-crystalline phenomena [1]).

These experiments were repeated with a second cobalt ellipsoid, and the same asymmetric action was observed but somewhat weaker. But in this case a disturbance of another nature was encountered, which shows how much the concomitant disturbing phenomena may affect the measurement of magnetization: the magnetization at low temperature was now found to be apparently smaller than at ordinary temperature. The following table contains an extract from the results obtained with this ellipsoid.

TABLE V.

Cobalt II at $t = 18°$ *C.*

H_e (gauss)	I^2 (cm. of scale)	Calc. zero	Obs. zero
4025	20.33	77.56	
12075	54.16	76.49	77.70
23340	59.76	76.86	
25560	59.94	76.90	

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[1]) P. Weiss, Arch. des Sc. phys et nat. février 1910, Journ. de phys. mars 1910.

Cobalt II in H_2 at atm. pressure (20°.3 *K.*)

15080	53.53	76.61	
23340	58.09	77.07	78.90
25650	58.46	77.21	

The same ellipsoid was removed from the holder and replaced with Khotinsky cement; one could easily understand that very strong strain-magnetic phenomena might be occasioned by forcibly driving it into its mount. At the same time for the new experiment it could be placed under a different angle by rotation with respect to its major axis; by this operation the sign of the change of zero point as a function of the field was reversed.

TABLE VI.

Cobalt II $t = 16°.5$ *C.*

H_e (gauss)	I^2 (cm. of scale)	Calc. zero	Obs. Zero
8050	40.99	79.12	
19560	56.48	78.80	79.45
23340	57.07	78.89	
25650	57.34	78.90	

Cobalt II in H_2 at atm. pressure (20°.3 *K.*)

8050	34.07	78.88	79.20
19560	53.21	78.24	
23340	54.26	78.33	
25650	54.63	78.42	

The only conclusion one seems to be able to draw from these experiments with cobalt seems to be that the increase in magnetization of cobalt between ordinary and liquid hydrogen temperatures is very much smaller than that undergone by magnetite and nickel, for, if this were not the case, the increase could not have been obscured by the disturbing influences.

TABLE VII.

Iron.

H (gauss)	I^2 (cm. of scale) $t = 20°$ C.	$T = 20°.3$ K. (H_2 atm. press.)	$T = 14°.0$ K. (H_2 solidifying)
1700	95.23	101.98	101.95
5675	98.47	102.85	
8680	98.65	103.01	
13160	98.91	103.31	
15700	99.04	103.31	103.23
16940	99.08	103.27	
18360	99.06	103.27	
19250	99.07	103.25	103.25

for $H =$	$\frac{I_{20°.3 \text{ K.}}}{I_{20° \text{ C.}}} =$
19250	1.0209
18360	1.0210
16940	1.0209
15700	1.0213
mean not corrected for dilatation	1.0210

In all the iron experiments the zero as deduced by taking the mean of the readings to right and left remained remarkably constant. As a rule its displacement was only a few tenths of a millimetre in any one series, and 6 mm. in proceeding from one series to another.

The few measurements at the temperature of solidifying hydrogen are sufficient to show that nothing particular happens between 20° K. and 14° K.

Magnetite.

We have already mentioned that the preparation of magnetite by heating the sesquioxide needs an extremely high temperature if one wishes to make sure that the last traces of oxygen are removed. A first ellipsoid obtained from iron oxide that had been insufficiently heated exhibited only little more that one half of the magnetization that was expected; it showed, too, a very distinct hysteresis, which was about three times as great at liquid hydrogen temperature as at ordinary temperature, while in all the experiments with the other substances hysteresis phenomena were insignificant. Moreover, the magnetization of this substance was the same at ordinary and liquid hydrogen temperatures, while between them it reached a maximum.

These peculiarities were not displayed by a second ellipsoid cut from well heated magnetite, but with this second ellipsoid further phenomena were observed which have not yet been explained but which seem to be of secondary importance. The zero point deduced from the mean of the two scale readings differed noticeably from the observed zero, while in any one series of measurements at the same temperature it remained practically constant. Further — and this is stranger — the deviations differ according to the direction of the field. It would clearly be very rash to attempt to ascribe to magnetite a hemimorphous symmetry like that of tourmaline from this sole observation. It seems more probable that some experimental error has here escaped our notice, and this can the more readily be accepted seeing that magnetite gives results much less regular than those of the metals. The following table contains an extract from the observations; the observations for the positive and negative directions of the field are given separately.

TABLE VIII.

Magnetite.

$t = 15°.8$ C

Observed zero = calculated zero + 0.9 cm.

H (gauss)	+ Field I^2 (cm. of scale)	— Field I^2 (cm. of scale)
8600	71.40	71.72
18100	71.83	72.00
21800	71.95	72.57
23300	71.99	72.57
24200	71.77	72.45
H_2 under atm. pressure (20°.3 K.)		
8600	79.78	79.88
18100	80.69	80.79
21800	80.73	80.96
23300	80.34	81.10
24200	80.08	81.37

H_2 solidifying (14°.0 K.).

18100	80.90	81.10
21800	81.12	81.64
24200	80.96	81.84

From these numbers follow these ratios of the intensities at 20°.3 K. and 15°.8 C.

TABLE IX.

H gauss	Field + $\frac{I_{20°.3K.}}{I_{15°.8C.}}$	Field — $\frac{I_{20°.3K.}}{I_{15°.8C.}}$
8600	1.0559	1.0553
18100	1.0591	1.0601
21800	1.0593	1.0567
23300	1.0564	1.0572
24200	1.0563	1.0628
mean	1.0574	1.0564

Hence $\frac{I_{20°.3K.}}{I_{15°.8C.}} = 1.0569$ not corrected for dilatation.

Similarly for the ratio of the magnetization at 14°.0 K. to that at 15°.8 C. we find

1.0609 1.0622

hence

$$\frac{I_{14°.0K.}}{I_{15°.8C.}} = 1.0616 \text{ not corrected for dilatation,}$$

a ratio which deviates from the foregoing in the expected direction.

Collecting the foregoing results we find in this branch of the research for the ferromagnetic substances omitting the correction for dilatation (see note 2 p. 14).

Nickel $\frac{I_{20°.3K.}}{I_{17°.3C.}} = 1.0548$

Iron $\frac{I_{20°.3K.}}{I_{20° C.}} = 1.0210$

Magnetite $\frac{I_{20°.3K.}}{I_{15°.8C.}} = 1.0569.$

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 115.

C. A. CROMMELIN. "Isotherms of monatomic gases and of their binary mixtures. IV. Remarks on the preparation of argon. V. Vapour pressures above — 140° C., critical temperature and critical pressure of argon." (*With a plate*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, **29 April 1910**, p. 924—936.)

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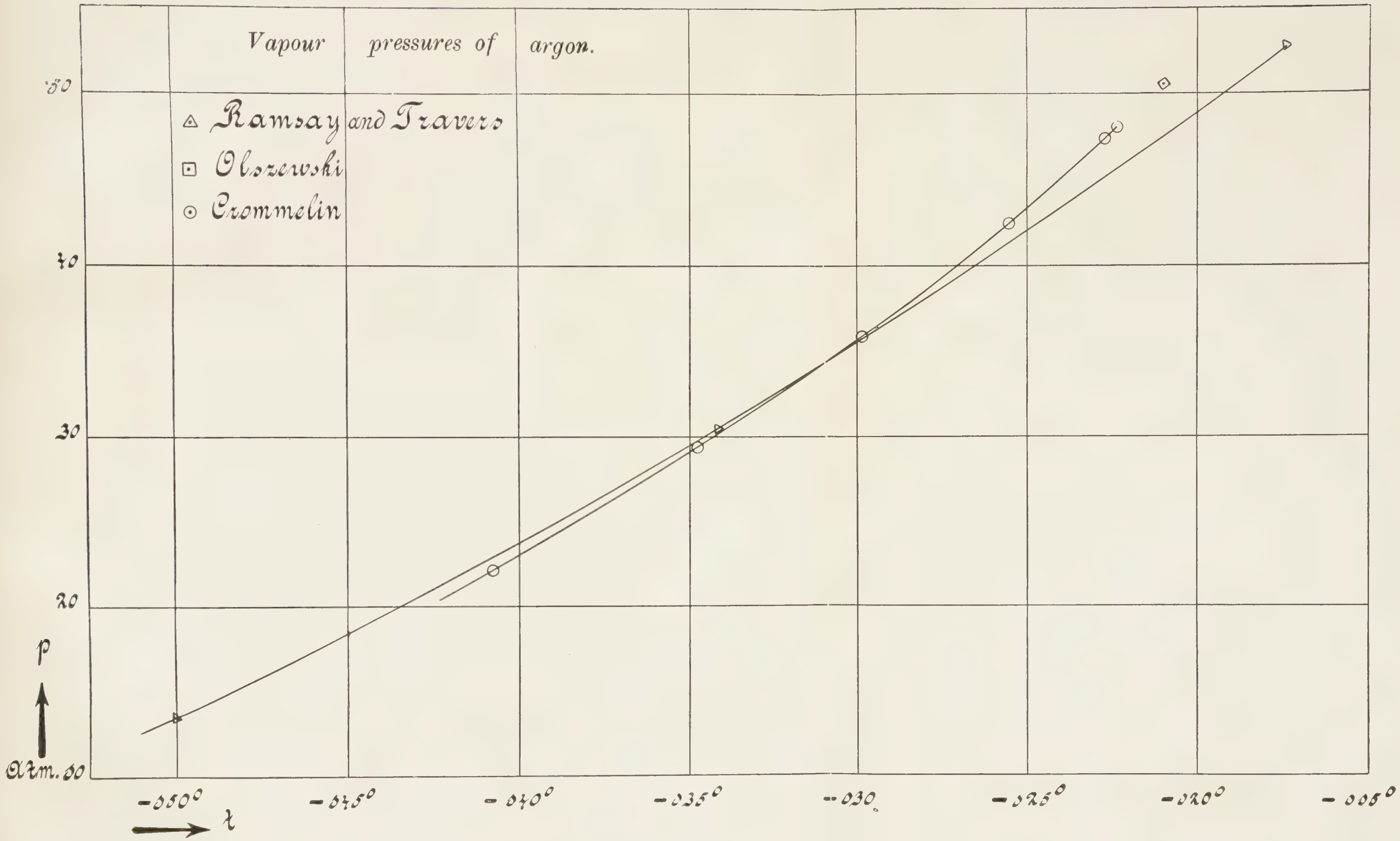
C. A. CROMMELIN. Isotherms of monatomic gases and of their binary mixtures. IV. Remarks on the preparation of argon. V. Vapour pressures above —140° C., critical temperature and critical pressure of argon."



Communication N°. 115.

C. A. CROMMELIN. — "*Isotherms of monatomic gases and of their binary mixtures.* IV. *Remarks on the preparation of argon.* V. *Vapour pressures above* – 140° *C., critical temperature and critical pressure of argon.*"

IV. *Remarks on the preparation of argon.*

§ 1. *Purely chemical methods.* The most important problem encountered in the preparation of argon is the removal of nitrogen from a mixture of argon and nitrogen. The chief substances that have up to the present come into prominence as absorbents of nitrogen are calcium, a mixture of calcium carbide and calcium chloride and a mixture of quick lime, magnesium and sodium.

a. Calcium. According to MOISSAN and RIGAUT [1]) calcium at a dark red heat readily unites with nitrogen to form calcium nitride (Ca_3N_2), while according to SODDY [2]) calcium unites with nitrogen (and also with all other gases except the monatomic) only at temperatures far above those that can be reached with the ordinary chemical combustion furnace.

According to my own experience calcium at a light red heat in a chemical combustion furnace unites but sluggishly with nitrogen. For this experiment I used an apparatus built upon the lines of that used by RAYLEIGH and RAMSAY [3]) in which the gas was passed in a cycle through the furnace by means of a continuous action mercury circulating pump. That nitrogen really united with calcium was shewn not only by the diminution of the pressure in the apparatus, but also by the calcium nitride that came from the tube after the experiment, a yellow substance (not brown, as is stated in some chemical text-books) that in the damp smelt strongly of ammonia This method did not lead to satisfactory results.

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[1]) H. MOISSAN and A. RIGAUT. Ann. de Chim. et de ph. (8). 2. 433. 1904.

[2]) F. SODDY, Proc. R. S. Nov. 15th 1906, excerpt in Nature Jan. 24th 1907.

[3]) LORD RAYLEIGH and W. RAMSAY, Phil. Trans. R. S. (A). 186. 187. 1895.

b. Mixture of 90% *calcium carbide and* 10% *calcium chloride.* Fischer and Ringe [1]) have interested themselves in this method. It has the great advantage that oxygen and nitrogen are absorbed at the same time. In collaboration with Mr. H. Filippo, Chem. Docts., to whom I take this opportunity of expressing my warmest thanks for his invaluable assistance, I constructed an apparatus which enabled us to prepare a large quantity of crude argon in a short time. A description of the peculiarities of this apparatus may well be omitted; it was arranged so that larger quantities of air could be treated than was possible with that of Fischer and Ringe. With 1 K.G. of the mixture we treated about 216 L. of air, while Fischer and Ringe only managed about 180 L. I can well recommend this method for the preparation of large quantities of crude argon.

c. A mixture of 20 *parts by weight of quick-lime,* 4 *of magnesium and* 1 *of sodium.* This mixture recommended by Hempel [2]) as a modification of the Maquenne [3]) mixture I shall call the Hempel mixture; if prepared with great care it will be found to be of great service in the separation of nitrogen from crude argon. I used it for the final purification of the argon that was to be used for quantitative measurements.

The analysis of the gas obtained [4]) shewed the excellence of this mixture as an absorbent.

As far as I am aware, there are no determinations of the *dissociation-pressure* of magnesium- and calcium nitride at the temperature at which we worked. By heating the residue left from an experiment with Hempel mixture in a porcelain tube with ground joints, and attaching to one end a mercury-manometer for low pressures and to the other a Töpler pump I was unable to find any evidence of a dissociation-pressure with a cathetometer on which $^1/_{20}$ mm could be read with certainty. The dissociation-pressure is, therefore, certainly smaller than $^1/_{20}$ mm. Hence, under the most favourable circumstances there must not remain more than $^1/_{15000}$ nitrogen in the mixture.

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[1]) F. Fischer and O. Ringe, Chem. Ber. 41. 2017. 1908.

[2]) W. Hempel, Gasanalytische Methoden 3th Ed pg. 150.

[3]) L. Maquenne, C. R. 121. 1147. 1895.

[4]) See V, § 4. of this communication.

§ 2. *Electrochemical methods.* The union of nitrogen with oxygen under the influence of electric discharges which was employed by Rayleigh and Ramsay [1]), Rayleigh [2]), Becker [3]), and others in the preparation of argon is especially useful for removing the last traces of nitrogen. The great difficulty inherent in this method — its slowness — is partially overcome by the use of a transformer for high tension alternating currents instead of an induction coil. Following the principles of that used by Rayleigh and Ramsay I constructed an apparatus with transformer with great care for this purpose, and used it several times for a last purification. A flame arc between two fixed platinum electrodes was used as it was found in practice to be more suited to this purpose than the long narrow sparks [4]) which one would from a theoretical point of view probably choose [5]) in preference to a flame arc. To get an idea of the efficiency of the apparatus I made several measurements of the ratio between the watts consumed and the number of volt ampères in the low-tension circuit. This ratio is practically the same in both circuits of a well constructed transformer.

I found :

25 volts,
44 amps,
480 watts,

when the flame burned quietly. The ratio is therefore

$$\frac{480}{25 \times 44} = 0.44.$$

Seeing that I had no oscillograph available I had to leave unanswered the question if this unfavourable ratio was due to a large phase difference between current strength and potential (high inductive resistance), or to other causes (deformation of the current and potential curves as indicated by SCHEUER [1]), electromotive forces at the electrodes, etc.). Leaving this factor out of account, my apparatus gave an absorption of 11.8 L. per K. V. A. hour from a mixture of oxygen and nitrogen in the correct proportion to form nitric acid. RAYLEIGH [2]) absorbed 17.5 L. per K. V. A. hour.

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[1]) Lord Rayleigh and W. Ramsay, Phil. Trans R. S. (A.) 186, 187, 1895.

[2]) Lord Rayleigh, Journ. Chem. Soc. (Trans) 71, 181, 1897.

[3]) A. Becker, Ztschr. f. Electrochemie, 9, 600, 1903.

[4]) C. S. Bradley and R. Lovejoy, Ztschr. f. Electrochemie, 9, 868. 1903.

[5]) F. Haber, Thermodynamik technischer Gasreaktionen (München and Berlin Oldenbourg, 1905).

Ph. A. Guye, Conf. Soc. Chim. de France May 24th 1909.

§ 3. *Separation of argon and neon by fractional distillation.* The quantities of krypton, xenon and helium still present in the argon prepared [3]) according to one of the above methods could not influence the measurements (isotherms, vapour pressures) that were to be made with it. It was desirable, however, to get rid of the 0.1 or 0.2 % neon. This was done by fractionation at the temperature of liquid oxygen boiling under greatly reduced pressure (— 217° C.). This temperature is above the critical temperature of neon while extrapolation of the vapour pressures of solid argon measured by RAMSAY and TRAVERS [4]) by means of an equation of the form

$$\log p = A + \frac{B}{T}$$

gave me an estimate of 3 mm. as the value of the vapour pressure of solid argon at the temperature of — 217° C. This result which is in agreement with what the analogy of oxygen would lead us to expect was confirmed by the experiments themselves.

V. *Vapour pressures above — 140° C., critical temperature and critical pressure of argon.*

§ 1. The *object* with which these measurements were undertaken was two-fold: 1⁰. I wished to control the vapour pressure determinations of RAMSAY and TRAVERS [4]) and also the critical magnitudes found by RAMSAY and TRAVERS [4]) and by OLSZEWSKI [5]); and

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[1]) O. SCHEUER, Zeitschr. f. Electroch. 11. 565. 1905. Thesis for the doctorate. Genève. 1905.

[2]) RAYLEIGH, Journ. Chem. Soc. (Trans) 71.181, 1897.

[3]) M. W TRAVERS, Experimental studies of gases.

[4]) W. RAMSAY and M W TRAVERS, Phil. Trans. R. S. (A.) 197. 47, 1901.

[5]) K. OLSZEWSKI, Phil. Trans. R. S. (A), 186. 253. 1895.

2°. I wished, before proceeding to determine isotherms, to get an idea of the purity of the argon used by an application of KEESOM'S [1]) theory of the condensation of substances with small quantities of admixture.

§ 2. The *apparatus* with which the measurements were made was designed and used by KAMERLINGH ONNES and HYNDMAN for some unpublished researches on oxygen and it has already been noticed in a few words [2]).

To a great extent the apparatus corresponds with the piezometers of variable volume for low temperatures already described by KAMERLINGH ONNES and HYNDMAN [3]), with the exception that an alteration has been made in the small glass reservoir that was used for low temperatures and in the steel capillaries attached to it. This reservoir is 8 cm. long, has an internal diameter of 3.4 mm. and, particularly with a view to the observation of the critical phenomena, contains a glass stirrer. This stirrer can be moved up and down by means of a glass thread passing through the glass · capillary and attached to a similar stirrer enclosing a piece of soft iron that can be moved by means of a small electromagnet up and down in a small reservoir of the same dimensions above the capillary (where it projects above the cryostat). The lower reservoir is divided so that the position of the liquid meniscus may be read off and the motion of the meniscus may be followed.

As this piezometer was not intended for volume measurements and one is therefore not confined to one definite known quantity of gas (the normale volume) the steel capillary is provided with a steel T-piece to which a second capillary is soldered; in the middle of this capillary there is a steel high pressure valve; it connects the piezometer with a glass reservoir of argon the pressure in which can be raised to ± 1.5 atm. by mercury. In this way the range of densities that can be investigated with a single piezometer by the addition of gas is greatly extended.

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[1]) Comm. Phys. Lab. Leiden. No. 79 (1902).

[2]) Comm. No. 78 (1902) and Comm. No. 83 (1903).

[3]) Comm. No. 69 (1901).

At the time the dimensions of the piezometer were calculated for oxygen. Seeing that this substance has about the same critical constants as argon the piezometer can be used for argon without alteration.

The cryostat used was that constructed by KAMERLINGH ONNES in 1902 for apparatus of small dimensions and has already been described [1]).

The temperatures desired were reached by means of liquid ethylene boiling under reduced pressure, and the constancy of the temperature was regulated by a platinum resistance thermometer [2]).

The pressure was measured by a closed hydrogen manometer [3]) that had been calibrated with the KAMERLINGH ONNES [4]) open manometer. The accuracy of this pressure determination reached 1 in 3000.

The temperatures were measured by a platinum resistance thermometer constructed wholly of glass and platinum according to the directions of KAMERLINGH ONNES and CLAY [5]). This thermometer was compared with a standard resistance thermometer at a large number of temperatures between — 103° C. and — 140° C. The standard thermometer was very carefully compared with the hydrogen thermometer at various temperatures including — 102° C. and — 138° C. and a formula giving good agreement was calculated. Errors of a few hundredths of a degree may indeed occur in temperatures in the neighbourhood of — 120° C. and — 130° C. where there may be some doubt as to the magnitude of the deviations from the formula; but the temperatures are undoubtedly accurate to $^1/_{20}$ °. The temperatures calculated in this way on the scale of the hydrogen thermometer were reduced to the absolute scale by means of the corrections, given by KAMERLINGH ONNES and BRAAK [6]). The thermometer was calibrated and the temperatures were measured and calculated by Miss G. L. LORENTZ, phil. doct^a., to whom I take this opportunity of expressing my heartiest thanks for the valuable assistance she kindly gave me in my measurements. I am also indebted to Mr. W. J DE HAAS phil. doct^s. for his help in my determinations.

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[1]) Comm. N⁰. 83 (1903), where a drawing of the cryostat is to be found on plate IV.

[2]) Comm. N⁰. 83, § 5 (1903).

[3]) Comm. N⁰. 78, § 17 (1902) and Comm. No. 97*a*. § 3 (1907).

[4]) Comm. N⁰. 44 (1898).

[5]) Comm. N⁰. 99*b* (1907).

[6]) Comm. N⁰. 101*b* (1907).

§ 3. The *measurements* were made in the following fashion. After the formation of a small quantity of liquid the apparatus was left alone for some time to ensure temperature and pressure equilibrium, and then the position of the meniscus in the reservoir, the manometer, and the position of the meniscus in the glass stem of the piezometer were read off. The pressure was then raised sufficiently until the reservoir was almost filled with liquid when the measurements were repeated.

As is usual the critical temperature was approached gradually and then by steps of 0.1°. The fact that a temperature was below the critical was shewn by the occurrence of condensation with extremely slow compression (so as to make the adiabatic warming as small as possible and thus remain on the experimental isotherm). Being above the critical temperature was shewn by first raising the pressure above the critical and then lowering it by small expansions, of which the adiabatic cooling could be only a few hundredths of a degree; if while doing this no meniscus appeared then it was certain that the temperature was above the critical.

The pressure at which the meniscus disappeared at about the middle of the reservoir was taken to be the critical pressure.

For various reasons I gave up the idea of a searching investigation of the critical phenomena, and of a very exact determination of the critical constants. In the first place I suspected that my argon was not pure enough for that purpose, and this was confirmed later on by my measurements. In the second place since the description of the apparatus of KAMERLINGH ONNES and FABIUS [1]) the piezometer I used may be considered too antiquated for the purpose. The cryostat, too, left something to be desired in the constancy of the temperature.

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[1]) Comm. N^0. 98 (1907). More elaborate in G. H. FABIUS, Thesis for the doctorate, Leiden 1908, where drawings of the apparatusses are to be found.

§ 4. *Calculations.* The pressures and temperatures were first calculated, and then by means of **Keesom's** formula [1]) for the change of condensation pressure of a substance with small quantities of admixture an idea of the purity of the argon was obtained. I assumed, that the admixture, who could produce a perceptible increase of pressure, must be nitrogen, by far the greatest part. The experience collected in the preparation justifies this assumption.

Keesom's formula gives

$$(v_2-v_1)(p_1-p_2)=M\,RT\,x\,(e^k+e^{-k}-2)\ .\quad .\quad .\ (1)$$

in which

$$k=\left\{\alpha\frac{T}{p}\frac{dp}{dT}-\beta\right\}\frac{p\,(v_2-v_1)}{MRT}.$$

p is the vapour pressure of the pure substances at an absolute temperature T; p_2 and p_1 are the pressures at the beginning and end of condensation respectively, v_2 and v_1 are the molecular volumes of the vapour and liquid respectively; x is the required molecular proportion of admixture, and finally α and β are the two constants introduced by **Kamerlingh Onnes** [2]), viz:

$$\alpha=\frac{1}{T_k}\left(\frac{dT_{xk}}{dx}\right)_{x=0}$$

and

$$\beta=\frac{1}{p_k}\left(\frac{dp_{xk}}{dx}\right)_{x=0}.$$

This formula, however, is valid for the beginning and end of condensation, that is, for two corresponding points on the boundary curve (pv-diagram), while for experimental reasons I had arranged that my observations should be made just after the beginning and just before the end of condensation, that is, on two points on the experimental isotherm within the boundary curve.

To obtain a formula applicable to my measurements I, following a friendly hint given me by Dr. **Keesom**, worked on the two equations

$$\left.\begin{aligned}(v_2-v_1)(p_1-p)&=M\,RT\,.\,x\,.\,(e^{-k}-1)\\(v_2-v_1)(p_2-p)&=M\,RT\,.\,x\,.\,(1-e^{k})\end{aligned}\right\}\ ^{3)}$$

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[1]) Comm. N°. 79 (1902).

[2]) Comm. N°. 75. (1901).

[3]) Comm. N°. 79. (1902).

the difference between which gives equation (1), and obtained two other equations for points on the experimental isotherms in the neighbourhood of the boundary curve. These were

$$\left.\begin{aligned}(v_2 - v_1)(p_b - p) &= \frac{MRTx\,(e^{-k} - 1)}{1 + y_b - y_b\,e^{-k}}\\(v_2 - v_1)(p_a - p) &= \frac{MRTx\,(1 - e^{k})}{1 - y_a + y_a\,e^{k}}\end{aligned}\right\} \quad \ldots\ldots \quad (2)$$

in which

$$y_a = \frac{v_{a_2} - v_a}{v_{a_2} - v_{a_1}}$$

$$y_b = \frac{v_{b_2} - v_b}{v_{b_2} - v_{b_1}}.$$

In the new notation introduced a refers to a state shortly after the commencement and b to one shortly before the end of condensation; 1 refers to the liquid, and 2 to the vapour, all expressed in molecular volumes. From equations (2) we get for the relation between the difference between the initial and final pressure in my experiments and x:

$$p_b - p_a = \frac{MRTx}{v_2 - v_1}\left[\frac{e^{-k} - 1}{1 + y_b - y_b\,e^{-k}} - \frac{1 - e^{k}}{1 - y_a + y_a\,e^{k}}\right] \ldots (3).$$

This equation can be directly applied to my measurements for the calculation of x. One difficulty, however, arises from the occurrence of various magnitudes which in the meantime cannot be calculated with great accuracy, so that the values of x given below must be regarded as rather rough approximations, which, however, undoubtedly give the order of magnitude of x.

The greatest uncertainty is in the estimate of the values of the constants α and β for the proper calculation of which measurements with mixtures of argon and nitrogen are necessary. Seeing that as yet such measurements are wanting I followed KEESOM's [1]) method and by making various simplifying assumptions came to the following estimates:

$$\alpha = -0.216 \qquad \beta = -0.484$$ [2]).

The values of $\frac{T\,dp}{p\,dT}$ and of the vapour pressure of the pure substance were taken from the determinations made by RAMSAY and TRAVERS[1]), v_2 and v_1 were calculated from KEESOM's formula[2]) for coexisting liquid and vapour densities. To apply this formula I estimated the critical density from the liquid densities of argon given by BALY and DONNAN[3]) using the law of the diameter of CAILLETET and MATHIAS[4]) and the „loi du tiers" of MATHIAS[5]); the results given by these two methods were in satisfactory agreement.

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[1]) Comm No. 79. (1902).

[2]) For further values of α and β see J. E. VERSCHAFFELT, Suppl. N°. 10, (1904).

In this way I calculated the following values of x from three observations of the vapour pressure:

x	*Vol* %
0.00066	0.066
58	58
72	72

Considering how approximate values must be taken for various magnitudes occurring in equation (3) we may be well satisfied with this correspondence, and we may consider it as highly probable that the admixture is less than 0.1%

Making use of equations (2) and of the mean of the values given above for x I was able to reduce the observed vapour pressures to those of the pure substance.

These corrections are extremely small, and are only very little outside the limits of experimental accuracy. The critical magnitudes observed (true plait-point magnitudes) were corrected by means of the following two equations deduced by KEESOM[6]):

$$\left.\begin{aligned} &\frac{1}{T_k}\frac{dT_{pl}}{dx} = \alpha - \frac{\left(\beta - \alpha\frac{\partial\pi}{\partial\tau}\right)^2}{C_4\frac{\partial^2\pi}{\partial\omega\partial\pi}} \\ &\text{and} \\ &\frac{1}{p_k}\frac{dp_{pl}}{dx} = \beta - \frac{\partial\pi}{\partial\tau}\frac{\left(\beta - \alpha\frac{\partial\pi}{\partial\tau}\right)^2}{C_4\frac{\partial^2\pi}{\partial\omega\partial\tau}} \end{aligned}\right\} \quad . \; . \; . \; (4)$$

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[1]) W. RAMSAY en M. W. TRAVERS, Phil. Trans. (A) 197, 47. 1901.

[2]) Comm. N°. 79, pg 11. 1902.

[3]) E. C. C. BALY and F. G. DONNAN, Journ. Chem. Soc. 81, 911. 1902.

[4]) L. CAILLETET and E. MATHIAS, Journ. d. Phys. (2). 5, 549. 1886.

[5]) E. MATHIAS, Ann. d. l. Fac. d. Sc. Toulouse (6). 1892.

[6]) Comm. N°. 75. pg. 6. 1901.

in which $C_4 = \dfrac{MRT_k}{p_k v_k}$ and π, ω and τ refer to reduced magnitudes.

Assuming now with VAN DER WAALS [1]) that for all substances

$$\frac{\partial \pi}{\partial \tau} = 6.7$$

and with KEESOM [2]) that

$$C_4 \frac{\partial^2 \pi}{\partial \omega \partial \tau} = -32.2,$$

and also that we may write

$$\frac{dT_{pl}}{dx} = \frac{T_{pl} - T_k}{x}$$

and

$$\frac{dp_{pl}}{dx} = \frac{p_{pl} - p_k}{x}$$

and, finally, writing for T_k and p_k the observed magnitudes (hence really T_{pl} and p_{pl}), which assumption will only very slightly alter the very small corrections $T_k - T_{pl}$ and $p_k - p_{pl}$, equations (4) take the form:

$$T_k - T_{pl} = - T_{pl}\, x \left[\alpha - \frac{\left(\beta - \alpha \dfrac{\partial \pi}{\partial \tau}\right)^2}{C_4 \dfrac{\partial^2 \pi}{\partial \omega \partial \tau}} \right]$$

and

$$p_k - p_{pl} = - p_{pl}\, x \left[\beta - \frac{\partial \pi}{\partial \tau} \frac{\left(\beta - \alpha \dfrac{\partial \pi}{\partial \tau}\right)^2}{C_4 \dfrac{\partial^2 \pi}{\partial \omega \partial \tau}} \right].$$

From these equations I calculated the (very small) corrections for the critical magnitudes (+ 0.°02 C. and 0.009 atm.).

---

[1]) J. D. VAN DER WAALS, Proc. Apr. 1901.

[2]) Comm No. 75. 1901.

§ 5. *Results.* After reducing the observed results to those for the pure substance by the method shown in § 4 I obtained the following results.

Date	Series	t	p (atm.)
1910 10 Febr.	VI	—140°80	22.185
10 „	V	—134.72	29.264
9 „	III and IV	—129.83	35 846
9 „	II	—125.49	42.457
12 „	VIII	—122.70	47.503
14 „	IX	—122.49	47.890
Critical magnitudes			
14 Febr.	X.	—122°.44	**47.996**

These observations are shown graphically on the accompanying figure on which the pressures and critical point determined by Ramsay and Travers 1) and the Olszewski 2) critical point are shown for comparison.

The Ramsay-Travers critical point especially (—117°.4 C. and 52.9 atm.) deviates largely from mine, and this may perhaps be explained by the primitive method in which these experimenters had arranged their temperature bath.

§ 6. *Representation of the vapour pressure curve by empirical formulae.* I attempted to represent the results given in the previous section by Rankine 3) formulae.

A two constant formula, viz.:

$$\log p = A + \frac{B}{T},$$

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1) W. Ramsay and M. W. Travers, Phil. Trans. (A) 197, 147. 1901.

2) K. Olszewski, Phil. Trans. (A) 186. 253, 1895.

3) W. J. M. Rankine, Edinb. New. Phil. Journ. 1849 and Phil. Mag. 1854, Misc. Scient. Papers pgs. 1 and 410.

identical with the well-known VAN DER WAALS [1]) vapour pressure formula, in which but one of the constants is determined by the vapour pressures in order that the formula may give the observed critical pressure for the observed critical temperature did not give very satisfactory results; this may be seen from the following table in which $p(O)$ represents the observed pressures and $p(C)$ the calculated:

Series	$p(O)$	$p(C)$	$p(O) - p(C)$
VI	22.185	21.642	+ 0.543
V	29.264	28.841	+ 0.423
III and IV	35.846	35.697	+ 0.149
II	42 457	42.628	— 0.171
VIII	47.503	47.521	— 0.018
IX	47.890	47.903	— 0.013

A much better correspondence with the observations was given by a three-constant formula:

$$\log p = A + \frac{B}{T} + \frac{C}{T^2} \quad \ldots \ldots \ldots \quad (5)$$

which is identical with the vapour pressure formula given by KEESOM [2]) and has two constants to be determined by the vapour pressures. Calculating the constants by the method of the least squares I found

$$\left.\begin{array}{l} A = + 4.661764 \\ B = - 524.3169 \\ C = + 11343.28 \end{array}\right\} {}^{3)} \quad \ldots \ldots \ldots \quad (6)$$

which give the following correspondence with observation:

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[1]) J. D. VAN DER WAALS Cont. I (2d edition) pg. 158.

[2]) Comm. No. 88, 1904, pg. 53.

[3]) These and the following figures differ somehow from those of the original Dutch publication. The differences are due to an improved calculation.

Series	$p(O)$	$p(C)$	$p(O) - p(C)$
VI	22.185	22.210	— 0.025
V	29.264	29.172	+ 0.092
III and IV	35.846	35.856	— 0.010
II	42.457	42.674	— 0.217
VIII	47.503	47.526	— 0.023
IX	47.890	47.905	— 0.015

Owing to the paucity of experimental data I did not calculate the constants for a four-constant formula (three dependent upon the vapour pressures).

Equation (5) with the constants (6) give

$$\frac{T_k}{p_k}\left(\frac{dp}{dT}\right)_k = 5.712\ ^{1)}.$$

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1) See H. Happel, Ann. d. Phys. (4) 21, 342, 1906, and Phys. Ztschr. 10. 1026. 1909.

G. van Rij, Thesis for the doctorate. Amsterdam, 1908, pg. 13 sqq.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 116.

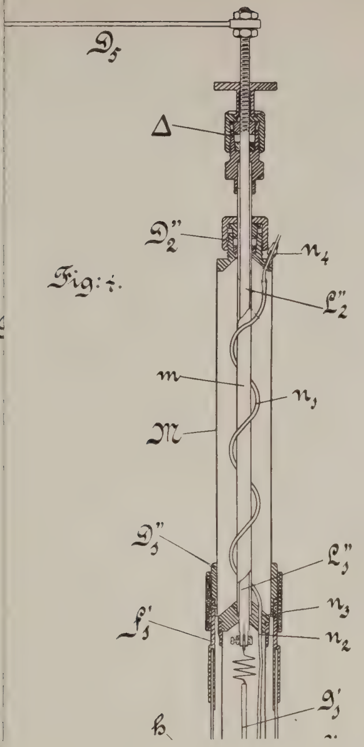
H. KAMERLINGH ONNES and **ALBERT PERRIER.** "Researches on the magnetization of liquid and solid oxygen." (*With a plate.*)

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, **29 April 1910** pp. 937—973.)

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLI

Fig: 7.



H. KAMERLINGH ONNES and ALBERT PERRIER. "Researches on the magnetization of liquid and solid oxygen."

Fig 1.

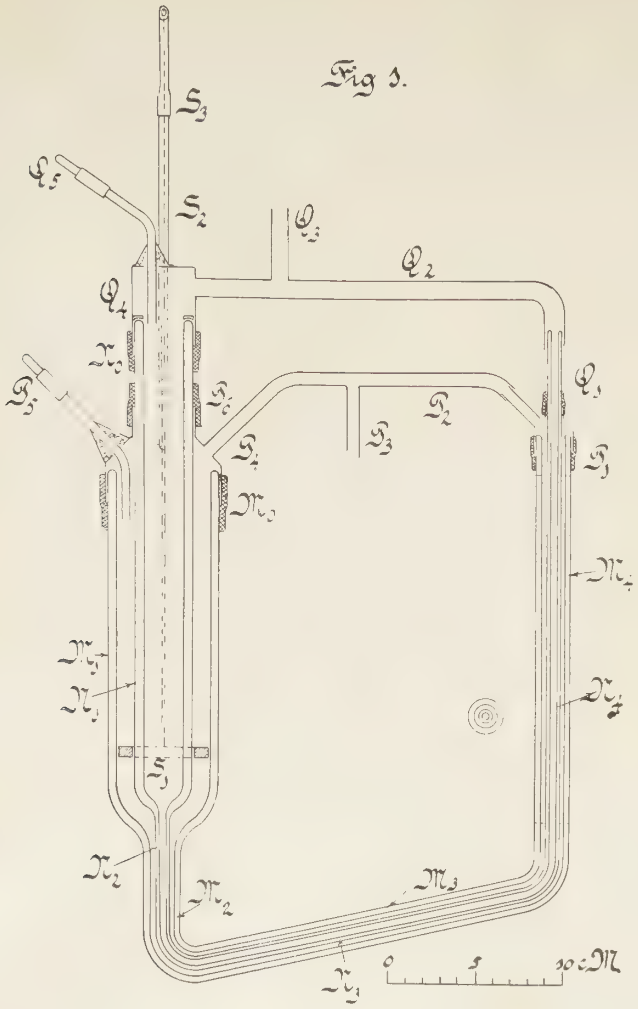


Fig: 2.

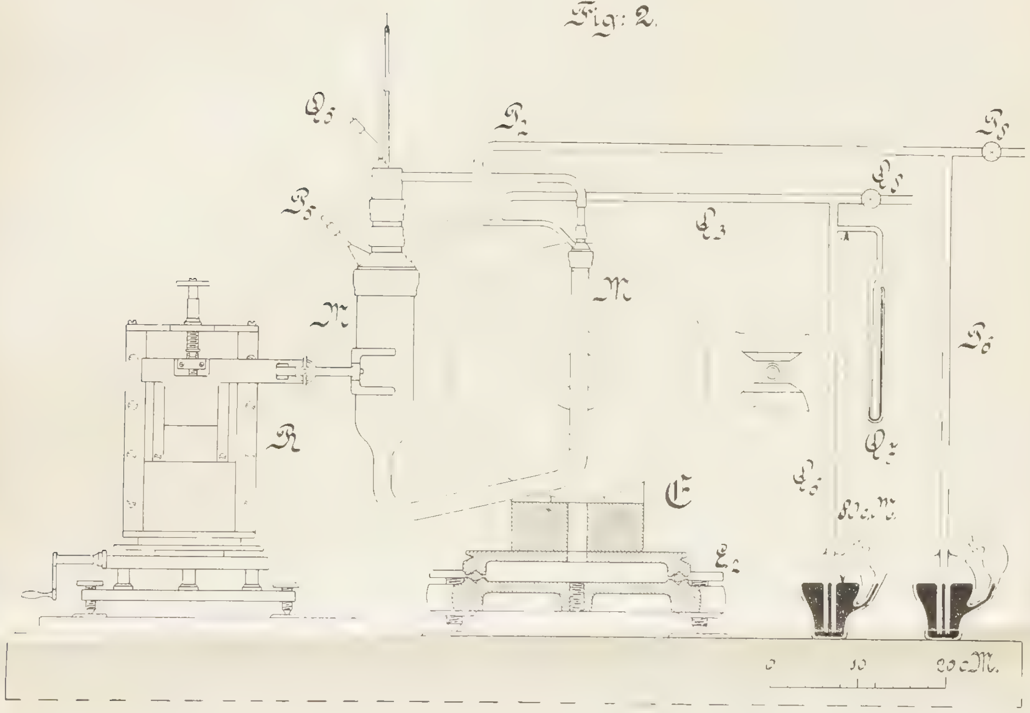


Fig: 3.

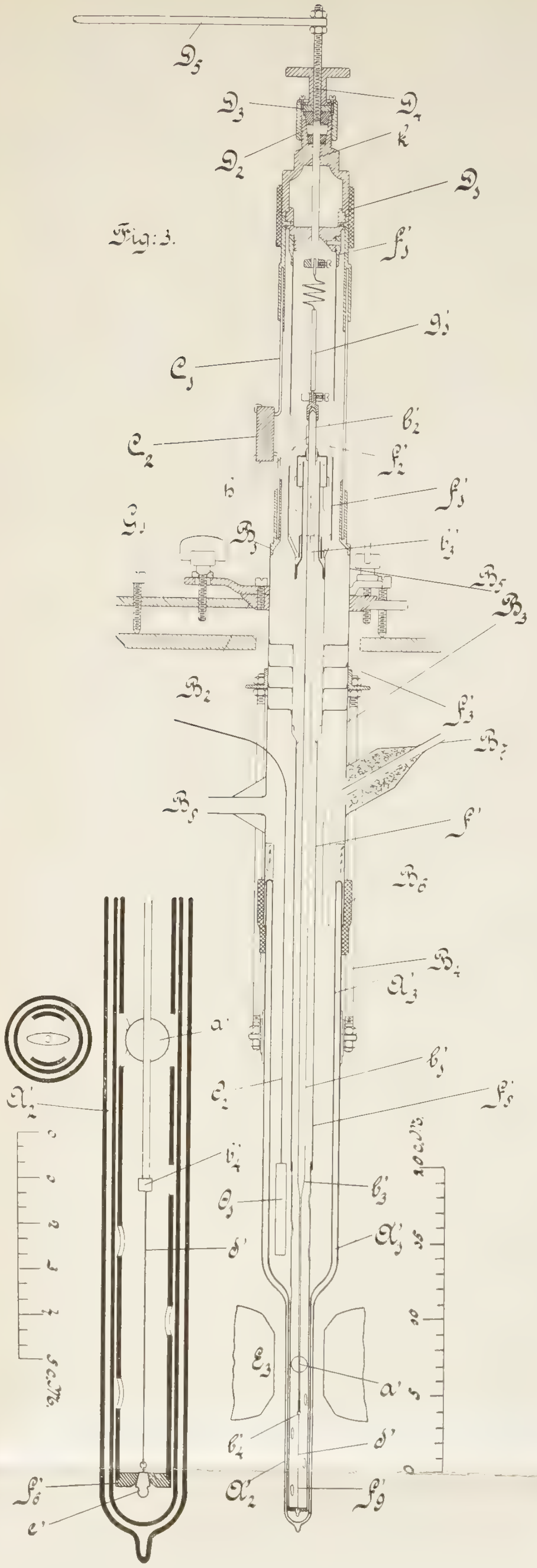


Fig: 4.

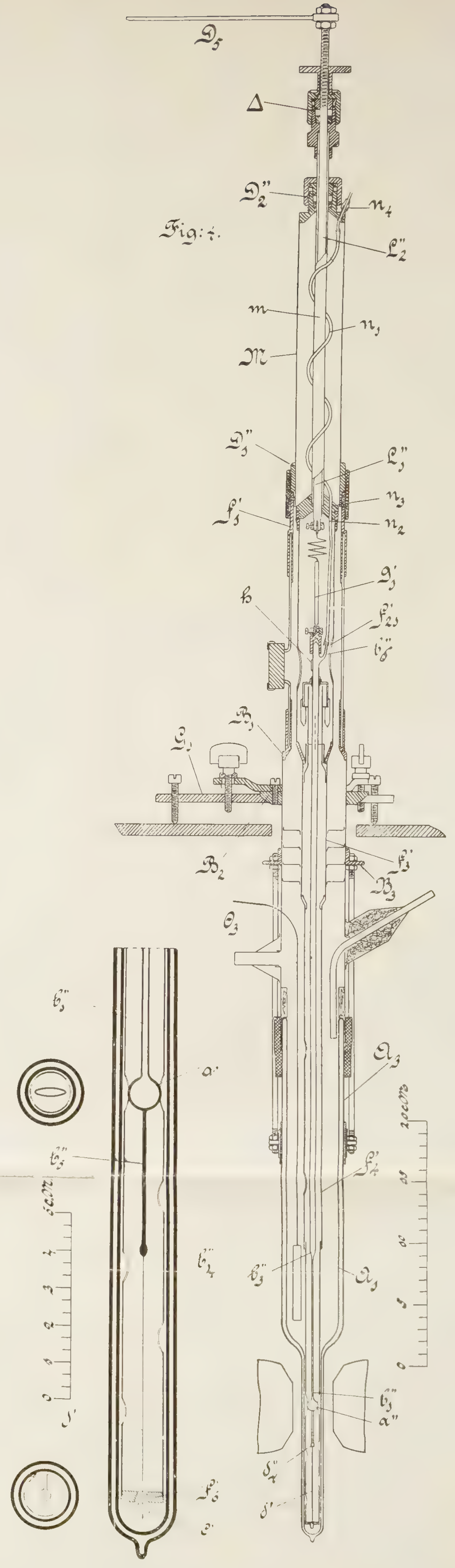
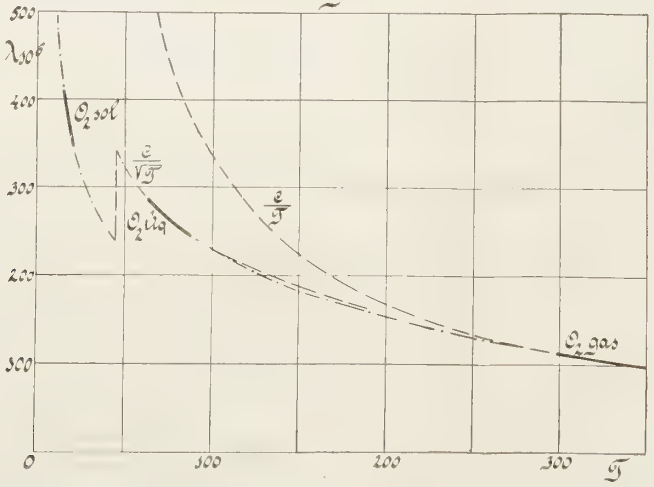


Fig: 5.



Communication No. 116.

H. KAMERLINGH ONNES and ALBERT PERRIER. — "*Researches on the magnetization of liquid and solid oxygen*".

§ 1. *Introduction.* It is scarcely necessary to remark that the investigation of the magnetic properties of oxygen at low temperatures has long occupied a position on the programme of the cryogenic laboratory, or that this has been considered one of the most important items on the programme since the investigation of both liquid and solid oxygen has been made possible by the perfecting of the methods [1]) of obtaining detailed series of measurements at constant temperatures in the region of liquid hydrogen. Indeed, while the strongly magnetic properties of oxygen of themselves select it from all other substances as especially suitable for the study of para-magnetism, we can in the meantime for no other substance obtain the *magnetic equation of state* [2]), which gives a representation of the magnetic properties of a substance in the three states of aggregation at as many successive temperatures and pressures as possible.

The investigation of oxygen at very low temperatures and at pressures that can easily be realised was expected to give at once results of much importance.

Curie [3]) found for gaseous oxygen between 20° C. and 450° C. that the *specific susceptibility* (magnetization per gram for $H = 1$) was inversely proportional to the absolute temperature, and Fleming and Dewar [4]) concluded from their latest measurement of the susceptibillity of liquid oxygen at its boiling point that Curie's law was obeyed down to —183° C.

Does the specific susceptibility continue to increase so strongly at low temperatures or does it approach a limiting value? Is oxygen in the solid state ferro-magnetic? Does the magnetization finally at extremely low temperatures perhaps begin to decrease and disappear completely at the absolute zero? [1])

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[1]) H. Kamerlingh Onnes. Comm No. 94*f* (1906).

[2]) H. Kamerlingh Onnes. Comm. Suppl. No. 9 p. 28.

[3]) P. Curie. Ann chim. phys. (7) 5 (1895) p. 289.

[4]) Fleming and Dewar. Proc. Royal Soc. London 63, p. 311, 1898.

These are questions which, considering the possibility of obtaining important contributions to the knowledge of the influence of density upon susceptibility by high pressures in the region where the gaseous state of aggregation changes continuously into the liquid make it a very attractive work to realise, even from a purely experimental point of view, the representation to which we have just referred.

The work was commenced though only when Prof. WEISS extended his magnetical researches to very low temperatures and the measurements on the magnetization of ferro-magnetic and cognate substances at very low temperatures, which were communicated to the February Meeting [2]), were undertaken. With that investigation which was carried out at the same time, the present one is very closely related, and for part of them we made use of the same appliances. In our present investigation we have also in various ways made use of Prof. WEISS's method [3]) of determining the magnetization by means of the maximum couple exerted by a magnetic field of variable direction upon an ellipsoid of the experimental substance, a method which had been entirely successful in the other research. We must also express the great advantage we derived from the continued support given us by Prof. WEISS, and we take this opportunity of gratefully acknowledging our indebtedness to him.

The change with temperature of the specific susceptibility of oxygen, the investigation of which was our first object, is of particular importance seeing that CURIE's law follows from LANGEVIN's kinetic theory of magnetism [4]). It was soon apparent to us that this law was not valid for oxygen, as was thought, down to — 183° C., but that it would have to be replaced by another. According to the important paper of du Bois and Honda communicated to the January Meeting — our experiments had already been completed at that time — various elements were found for which Curie's law did not hold at temperatures above 0° C. This at once increases the importance of the further investigation of oxygen, for which over a definite region of temperature Curie's law is valid, while over another region it obeys a second law, viz.: *that of inverse proportionality to the square root of the absolute temperature.* The results concerning this law and also concerning the probability of a *sudden change in the value of the specific susceptibility on solidification* will be discussed in § 5.

---

[1]) It has since appeared that the magnetization of ferro-magnectic substances does not yet give any justification when the temperature is lowered to the melting point of hydrogen for the assumption that the electrons whose motion causes magnetization are frozen fast to the atoms and that therefore this disappearance at the absolute zero may be expected. (P. WEISS and H. KAMERLINGH ONNES, Comm. No. 114 p. 9).

[2]) P. WEISS and H. KAMERLINGH ONNES. Comm. No. 114 (1910).

[3]) P. WEISS. Journ. de phys. 4e série t. VI, p. 661; 1907.

[4]) LANGEVIN. Ann. chim. phys. (8) 5, p. 70; 1905.

We have been occupied with another question besides the change of specific susceptibility with temperature, which was suggested both by the experimental results obtained by Fleming and Dewar and by the theories of Langevin and Weiss.

In the experiments of the first-named there appears sufficient evidence for the conclusion that there is a decided diminution of the susceptibility as the strength of the field increases (the diminution is of the order of 10% in a field of 2500 gauss). Now, according to the theory of Langevin para-magnetic substances must, it is true, exhibit this phenomenon, but calculation from his formulae limits the magnitude of this change to less than 0.1% in the case of liquid oxygen at its boiling point. Should a higher value than this be obtained, then one would be led to assume the existence of a Weiss molecular field [1]). We arranged our experiments so that the liquid and the solid oxygen could be subjected to a field of 16000 gauss, a field very much stronger (about six times) than that used by Fleming and Dewar, so that we might expect the phenomenon which appeared in the course of their experiments to be exhibited to a much greater degree in ours even at the same temperatures as were used by them. If what was observed by Fleming and Dewar could really be ascribed to the beginning of saturation then the theory would further lead us to expect that as the temperature sank the change would strongly increase (becoming infinite at $T = 0$), and that in our experiments with liquid hydrogen it would become very striking. We have, however, observed only small deviations, which we shall discuss further in § 5.

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[1]) Weiss, L'hyp. du champ. moléc. loc. cit.

As regards the experimental methods employed by us in our investigation, two completely different schemes were adopted: on the one hand was measured the magnetic attraction exerted upon a column of the liquid, and on the other the maximum couple exerted by a homogeneous field upon an ellipsoid. The second method is more especially suitable for comparative measurements and can also be used for frozen oxygen; the first can be used only for the liquid phase, but on the other hand it makes very trustworthy absolute measurements possible; we have therefore adopted it as the basis of our other measurements. In the carrying-out of each method further precautions are still desirable, so that while we are busy pushing on the investigation, we propose at the same time to repeat it in part in order to increase the accuracy of the results obtained by taking such further precautions as have appeared possible in the course of the work.

Liquid oxygen I.

§ 2 *Method of the magnetic rise.* As mentioned above, we have rendered the method of the magnetic rise employed by QUINCKE, DU BOIS and other observers suitable for use at low temperatures.

One limb of a vertical O-shaped tube, the upper portion of which contains the gaseous, and the lower the liquid phase of the experimental liquefied gas was placed between the poles of a magnet whose field was horizontal.

Let H be the field, (H' the field in the other limb is supposed to be so small that $(H'/H)^2$ is negligible), g the acceleration due to gravity, z the difference in height of the levels of the liquid under the influence of H, ρ and ρ_0 the densities of the liquid and of the gaseous phases respectively, K and K_0 their respective volume susceptibilities, then

$$(K-K_0)\,H^2 = 2z\,(\rho-\rho_0)\,g \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or, by introducing the absolute specific susceptibility χ

$$(\chi\rho-\chi_0\rho_0)\,H^2 = 2z\,(\rho-\rho_0)\,g.$$

If $\varkappa = \varkappa_0$ then the equation becomes simply

$$\varkappa = \frac{2zg}{H^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is the formula we have used for our calculations. [1])

So there are striking advantages offered by this method particularly for an absolute measurement, on account of its applicability to the case of a liquid in equilibrium with its own vapour. There are only two magnitudes to be determined, the distance z, which can be measured very accurately with a cathetometer, and the field H; nor have we to know the density of the liquid in order to be able to find the specific susceptibility.

Magnetic rise apparatus. It is a very easy matter to cause an ordinary liquid to ascend under the influence of magnetic attraction, but the experiment is attended by serious difficulties when one has to deal with a liquefied gas. Boiling must be completely avoided, and care must be taken that the vaporization is unnoticeable. The first precaution is necessary because the motion of the liquid or of its surface would render adjustment quite impossible, and the second is necessary so that the total quantity of liquid may not appreciably alter during the measurement of one rise. Moreover magnetic action itself increases the difficulties; it is easy to see that it can occasion the formation of gas-bubbles which divide the column of liquid into two parts, so that the one portion remains suspended between the poles, while the other falls back again. In that case measurement of the ascent is out of the question.

Starting from the thermodynamic potential it appears that in every case the relation.

$$2g\, y\, \rho > K\,(H^2 - H_y{}^2)$$

must hold, where H is the field at the surface of the liquid, and H_y the field at a distance y below the surface of the liquid. These conditions show that there is a limit to the intensity of the fields in which measurements may be made, for they necessitate a range of extended fields (in this case in a vertical direction). Conical pole-pieces are thus automatically barred.

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[1]) In § 5 we shall give the reasons why we think that $\chi = \chi_0$, and should it be possible that this is not the case there is still the greatest probability that $\chi_0 < 1.5\,\chi$; in the most unfavourable case at the boiling-point the correction remains below 0.002 in value, while at lower temperatures it is quite negligible on account of the small value of ρ_0.

After several preliminary experiments an apparatus was constructed, the most important part of which consisted of two concentric doublewalled vacuum tubes, with which we already succeeded in obtaining rather successful measurements. The walls of the double vacuum tube were not silvered, so that we were able to watch how the liquid behaved during the experiments. From the experience thus acquired the improved apparatus which we shall now proceed to describe was designed and constructed.

It will be seen that the construction of the apparatus lays a very heavy tax upon the art of the glass-blower [1]). As before, the chief part consisted of two independent U-shaped vacuum tubes, the one fitting inside the other. The double walls of each tube are completely silvered on the vacuum side, except in the case of the inner tube, where the distance which the liquid ascends is left free, and in the outer where a sufficient length is left unsilvered to leave a strip of a few millimeters breadth through which the level of the liquid can be read. One of the tubes completely surrounds that portion of the other which contains liquid; this we call the protecting tube. The narrowest portion M_4 (fig. 2) is placed between the poles of the electro-magnet. The narrow limb of the inner tube must of course be perfectly cylindrical. The other limb is enlarged and serves as a reservoir. In order to be able to apply equation (2) all care was taken that the temperature of the liquid and vapour up to a height somewhat greater than that reached by the column of liquid was everywhere the same both in the wide and in the narrow tube; and further care was taken that where the temperature of the vapour above the liquid in the upper parts of the apparatus changes to ordinary temperature it was as far as possible the same at the same height in the two limbs of the O-shaped space. With this end in view the liquid in the inner tube was, by means of the magnetic field, repeatedly moved up and down under constant vapour pressure, until we might assume that in this tube equilibrium was sufficiently well attained. To make this equilibrium possible the inner tube is surrounded with liquid at the same temperature as that which the liquid in it must attain. In the outer or protecting tube the liquid is kept constantly in motion by means of a stirrer consisting of a brass ring S_1 that can be moved up and down; it is possible to do this and still keep the space closed by utilising the flexible rubber tube S_2. The vaporization in the inner tube is thus very small (between 0.5 and 1 litre of gas measured under normal atmospheric pressure escapes per hour).

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[1]) The double vacuum tube was prepared by Mr. KESSELRING, Laboratory glassblower, and the remainder by Mr. FLIM, technical assistant at the Laboratory.

Notwithstanding all these precautions temperature differences must still be encountered. In the liquid, in which the convection currents maintaining heat-equilibrium can be followed by the small particles which they carry along with them, these temperature differences must have been very small. In the gas layer in the upper portion of the O-shaped space there must, however, have been considerable differences; but on account of the small density of the gas, these have but small influence upon the difference of level in the two limbs, and, moreover, that influence may be almost entirely neglected seeing that the observations are simply comparative measurements with and without the magnetic field. Now, care has been taken that the temperature over the distance that the liquid rises can vary but slightly, while in the upper portions of the tube practically the same state of affairs is maintained during both observations. We have therefore omitted the correction that should still have to be applied for possible temperature differences.

Comparing the positions of the liquid in the narrow cylindrical tube with and without the magnetic field also reduces the correction for capillarity to the insignificant differences in form of the menisci, and this correction, too, we have omitted.

The inner and the outer tubes are closed independently of each other by means of the German-silver caps P_1, P_4, Q_1, Q_4 (fig. 1); the junction is made air-tight by the rubber sleeves M_0, N_0, which at the same time unite the two tubes firmly together. Liquid oxygen is introduced into the protecting tube through the small tube P_5, and into the inner tube through Q_5. The two tubes P_3 and Q_3 lead the vaporized oxygen through the valves P_8 and Q_8 (fig. 2) to two gasometers. Two manometers P_6 and Q_6, the latter of which is provided with an indicator Q_7, so that small vapour pressures may be read off accurately, serve at the same time as safety valves. It is not necessary that the oxygen in the protecting tube should be as pure as that in the inner tube; for the latter, with which the observations were made, very pure oxygen was used.

A double sliding movement R allowed an easy adjustment of the apparatus each time, so that the meniscus in the measuring tube just reached the desired point in the field between the poles, usually in the axis of the pole pieces.

Course of a series of measurements. The field is brought to the desired strength and by means of R the meniscus is made rise to the desired point, which is read off on a small scale. Then the meniscus is moved up and down several times while care is taken that the field slowly increases. In this way the temperature is made everywhere the same and the walls of the tube are wetted. While the field has the desired value the position of the meniscus is read off; then a reading is made while the field is off; after the meniscus has been three times allowed to rise somewhat higher than the desired position, another reading is made while the field is on; once more a reading is made with the field off and so on several times. In this manner the error arising from vaporization of the liquid during the adjustment of the cathetometer is eliminated [1]). It is not essential to know the position of the level in the other limb of the tube; so as to be able to take account of this, we ascertained the ratio of the cross-sections of the two limbs of the tube.

We have further made sure that the residual magnetism exerted no appreciable influence upon the position of the meniscus after the current was cut off. For this purpose a feeble current was sent through the coils in the direction opposite to that which had just been broken. Had the residual field exerted any appreciable influence we should have seen first a further sinking of the level, and then a rise as the current was slowly increased. This has not been observed.

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[1]) To control the position of the meniscus without the magnetic field, we measured the quantity of gas vaporized (cf. preceding page).

We used the same electro-magnet as was used for the cryogenic investigation of the ferro-magnetic metals [1]), to which we must refer for details regarding its construction. It was only necassary to replace the conical pole-pieces by cylinders with flat ends. Their distance apart was micrometrically adjusted to 25 mm. and controlled with an accurate callipers. We may here remark that between the measurement of the ascent and that of the field, the pole-pieces remained clamped tight to the cores, so the adjustment of the distance could give rise to no error.

Since in the subsequent calculation the strength of the field is involved to the second power, and since we are concerned with an absolute measurement, we endeavoured to make our measurement of the field strength as trustworthy as possible with our present appliances. With this end in view we measured the strength of an arbitrarily chosen standard field, by two different processes and we compared the strengths of the fields used in our experiments with this standard by successively withdrawing the same coil attached to a ballistic galvanometer from the standard field and from the various fields which we desired to measure.

The standard field was set up with the same flat pole-pieces at a distance of 9 mm. apart, and with a current of 5 amp. All precautions were taken to ensure the demagnetization of the magnetic cycle beforehand. This field was first measured by means of COTTON's magnetic balance [2]). As is well known this method consists of equiliorating weights of a total mass m against the ponderomotive power of the field H on a straight portion of length l of a conductor through which a current flows of intensity i; then we get

$$H = \frac{m\,g}{i\,l} \cdot 10.$$

For the degree of accuracy, however, which we wish to reach several corrections must be taken into account. In the first place the various parts of the balance were accurately calibrated. The length l of the current element was determined micrometrically and on the dividing engine, and so also was the distance between the arcs of the balance which distance ought to be the same throughout seeing that the arcs must be accurately concentric. The very small deviations from this were allowed for by means of a ballistic investigation of the topography of the field. The balance arms of the weights and of the current element were measured with the cathetometer. The topographical study of the field also gave us the correction necessary for the force exerted upon the second straight element of the balance (i.e. that outside the pole-gap). The sum total of these positive and negative corrections came to some units per thousand.

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[1]) P. WEISS and H. KAMERLINGH ONNES, l. c.

[2]) For this method of measuring the field and for the magnetic balance see: P. WEISS and A. COTTON, Le phénomène de ZEEMAN pour les trois raies bleues du zinc, Bull. Séances Soc. franç. de phys. 1907, p. 140, also J. de phys. 1907.

The greatest care had to be devoted to the absolute value of *i* which was measured by means of an accurate ammeter by SIEMENS and HALSKE. This was calibrated in absolute ampères by comparing on the potentiometer the potential difference between the terminals of an international ohm (or for the stronger currents of 0.1 Ω) with the electromotive force of a WESTON cadmium cell. For the requisite accuracy of the measurements the influence of neighbouring instruments or currents upon the ammeter, or of its position in the earth's field were by no means negligible; we got rid of almost all these irregularities by a suitable adjustment of the distances and of the positions of the rheostats, and we eliminated further possible remaining errors by so connecting *all conductors* that the currents *in all* except the ammeters could be reversed *at the same time*. Finally we always used the ammeters in the same position with respect to the earth's field as that in which they had been calibrated.

When all calculations and corrections had been completed it was found that the strength of the standard field was 9857 gauss according to this method.

The *second method* by which the value of the same field was found consisted of the sudden withdrawal from between the poles of the magnet of a coil of wire of which the area encircled by the current was known. The change thus caused in the number of induction lines embraced by the coil was compared by means of a ballistic galvanometer with the number of induction lines embraced by a solenoid the dimensions of which were accurately known.

The coil consisted of 19 turns of silk-insulated wire, 0.25 m.m.

thick, wound round a cylinder of ebonite, 20 m.m. in diameter. The dimensions were obtained by various measurements with the micrometer screw and the dividing engine, and were repeatedly controlled. At the same time a control coil was constructed by winding bare copper wire in a helical groove cut in the curved surface of a cylinder of ebonite; the area encircled by the current was then measured for this control coil by the same methods and with the same precautions as were adopted in the case of the first. The ratio of the two was in agreement with the ratio of the deflections of the ballistic galvanometer which were obtained by connecting the two coils in series with the galvanometer and then withdrawing them successively from an unchanged magnetic field. We may further say that we had previously verified the absence of magnetic properties from the ebonite by means of an apparatus after CURIE in which we utilised the attraction in a non-uniform field.

For the measurement of the field there were placed in circuit with the galvanometer the coil on the ebonite cylinder, a manganin resistance to regulate the sensitivity, a secondary coil of 500 turns fitting round the standard solenoid, and finally, an electromagnetic arrangement which could be used as a damper if desired. We also allowed for the very small deviations from the law of proportionality between the deflections of the galvanometer and the quantities of electricity, which had been determined for the galvanometer (one of the DEPREZ-D'ARSONVAL type) by a previous investigation. The solenoid was constructed with the greatest accuracy by winding bare copper wire on a core of white marble [1]).

The standardisation of the galvanometer was made by reversing the current in the solenoid; the observations made by withdrawing the coil from the field always took place between two standardisations of the galvanometer; there was, however, no change in the galvanometer constant to be observed. The corrections and precautions necessary in obtaining the strengths of the current are the same as in the case of the balance, and have already been described. The final result of this ballistic method is 9845 gauss.

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[1]) For the dimensions and the description of the solenoid and galvanometer see: P. WEISS, Mesure de l'intensité d'aimantation à saturation en valeur absolue, Arch. Sc. phys. et nat. February 1910, also J. de phys. May 1910.

The relative difference between this and the value given by Cotton's balance is therefore 0.0012; and this can be neglected especially when one remembers that almost every one of the numerous measurements necessitated by the one method as much as by the other, beginning with the adjustment of the field by means of the ammeter, is accurate only to 0.0005. It may be useful to comment here upon a particular point that increases the difficulty of obtaining this agreement and therefore enables us to rely more upon the correctness of the numbers which we have obtained. The equation for Cotton's balance involves the strength of the current in the *denominator*, while this magnitude in calculating according to the ballistic method occurs in the *numerator*; a systematic error therefore in the *absolute* number of ampères would, of necessity, occasion a relative difference *twice as great* between the values of the field obtained by the two methods (the same ammeter was used with the balance and with the solenoid).

We have given the ballistic method a somewhat greater weight than the other on account of the smaller number of corrections it involved, and thus we have finally taken as the value of the standard field

9850 gauss.

Once this standard field was definitely fixed all other measurements could be rapidly made by the ballistic method described above.

For the conical pole-pieces which are employed in experiments according to the maximum couple method, and which give much more powerful but much less uniform fields, we used a coil of 7 to 8 mm. diameter accurately centred on the axis of the pole-pieces. In this case direct comparison with the standard field just mentioned was not possible since the flat pole-pieces had to be screwed off to make room for the conical poles. To meet this case the area of the small coil encircled by the current was determined once and for all by withdrawing it from the standard field *before* the flat pole-pieces were removed, and comparing the change thus brought about in the number of the induction lines with those of the solenoid by means of the ballistic galvanometer.

All the measurements that we have described up to the present refer to the field in the centre of the space between the poles.

For the few exceptional values of the field, and, consequently, of the ascent of the liquid oxygen for which it was necessary to cause it to rise pretty far above the axis of the pole-pieces, the field was determined at those points by simple ballistic comparison with the field on the axis, and we made use of the cathetometer to adjust the position of the small coil.

Results of observations and calculations.

Series of observations with the apparatus with unsilvered walls.

TABLE I*a*. $t = -183°.0$ C. [1]

Position of meniscus.	Obs. rise z' in cm.	Diff. in height with reservoir z in cm.	H in gauss.	$\frac{z}{H^2} . 10^7$
Level of axis	1.032	1.061	2980	1.194
„	1.646	1.690	3727	1.216
„	1.656	1.701	3727	1.224
axis + 2.44 cm.	3.024	3.110	5182	1.158
axis	3.198	3.289	5205	1.214
„	4.16	4.278	5848	1.251
axis + 2.44	4.90	5.050	6570	1.168
axis	5.124	5.270	6600	1.210
axis + 2.44	7.87	8.094	8075	1.242
axis + 2.44	9.20	9.462	9043	1.158*

The difference in height z was obtained from the observed ascent from $z = z' (1 + 0.0285)$. The observation * was very difficult and is little reliable.

The deviation in the case of the observation in a field of 5182 gauss is probably due to a mistake of 1 in the number of whole millimeters which were read off, but of this we are not certain.

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[1] The boiling point of oxygen according to H. KAMERLINGH ONNES and C. BRAAK, Comm. No 107a (1908) § 6.

Deviations from proportionality with H^2 are considerable but by no means systematic. If we take the mean of all the measurements with the exception of the last in which special difficulties were encountered we reach the value

$$\frac{z}{H^2} = 1.209 \,.\, 10^{-7},$$

and for the specific susceptibility with $g = 981.3$ for Leiden

$$\chi_{90^\circ.1\ \mathrm{K.}} = 237.3 \,.\, 10^{-6}:$$

TABLE *Ib*. $t = - 201^\circ.75$ C.

Position of meniscus.	Obs. rise z' in cm.	Diff. in height with reservoir z in cm.	H in gauss.	$\frac{z}{H^2} \cdot 10^7$
Level of axis	1.192	1.222	2980	1.376
„	1.893	1.944	3727	1.399
„	1.881	1.935	3727	1.393
„	3.643	3.747	5205	1.383
„	4.623	4.752	5848	1.389
„	5.91	6.078	6600	1.395
axis + 2.5 cm.	7.376	7.586	7421	1.378
axis + 2.5 cm.	8.715	8.963	8069	1.372

$$\text{mean} \quad \frac{z}{H^2} = 1.386.10^{-7}$$

whence it follows that $\chi_{71^\circ.35\ \mathrm{K.}} = 272.0.10^{-6}$.

Finally, at — 209°.2 C. a single observation was made. The rise was 6.115 cm. in a field of 6600 gauss, which with the correction for the sinking in the reservoir gives

$$\frac{z}{H^2} = 1.444.10^{-7} \text{ and } \chi_{63^\circ.9\ \mathrm{K.}} = 283.4.10^{-6}.$$

We shall now give the series of observations made with the silver-walled apparatus which we have already described.

TABLE II*a*. $t = -183°.0$ C.

Position of meniscus.	Obs. rise z' in cm.	Diff. in height with reservoir z in cm.	H in gauss.	$\frac{z}{H^2} \cdot 10^7$
axis	1.060	1.090	2980	1.227
"	1.669	1.716	3727	1.235
"	3.169	3.258	5183	1.213
"	3.220	3.310	5198	1.225
"	4.035	4.148	5807	1.230
"	4.093	4.208	5848	1.230
"	4.101	4.216	5848	1.233
"	5.119	5.262	6578	1.216
axis + 2.5 cm.	7.750	7.967	8075	1.224
"	8.950	9.201	8659	1.227
axis + 3.5 cm.	9.226	9.484	8808	1.222
"	9.266	9.525	8808	1.228

For this apparatus $z = z' \ (1 + 0.0280)$.

The mean value of $\frac{z}{H^2}$ is $1.226.10^{-7}$, whence it follows that

$$\chi_{90°.1 \text{ K.}} = 240.6.10^{-6}.$$

TABLE II*b*. $t = -201°.75$

Position of meniscus	Obs. rise z' in cm.	Diff. in height with reservoir z in cm.	H in gauss	$\frac{z}{H^2} \cdot 10^7$
axis	1.195	1.228	2980	1.383
"	1.879	1.932	3727	1.391
"	3.625	3.726	5205	1.375
"	4.567	4.695	5848	1.373
axis + 3.5 cm.	5.461	5.614	6399	1.371
axis + 2.5 cm.	5.832	5.995	6567	1.390
axis	5.852	6.016	6600	1.381
axis + 3.5 cm.	6.463	6.644	6986	1.365
axis + 2.5 cm.	6.899	7.092	7169	1.380
axis + 3.5 cm.	8.207	8.437	7863	1.365
axis + 2.5 cm.	8.654	8.892	8069	1.366
axis + 3.5 cm.	8.988	9.240	8212	1.370
axis	8.913	9.162	8212	1.358

Mean of all observations is 1.375, whence it follows that

$$\chi_{71^{\circ}35\ \mathrm{K.}} = 269.9\ .\ 10^{-6}.$$

TABLE IIc. $t = -208^{\circ}.2$ C.

Position of meniscus	Obs. rise z' in cm.	Diff. in height with reservoir z in cm.	H in gauss	$\frac{z}{H^2} \cdot 10^7$
axis	1.277	1.313	2980	1.478
"	1.996	2.052	3727	1.477
"	3.813	3.920	5205	1.447
"	4.841	4.977	5848	1.461
axis + 2.5 cm.	6.012	6.180	6567	1.433
axis	6.094	6.264	6600	1.438
"	6.113	6.284	6600	1.443
axis + 2.5 cm.	7.146	7.346	7169	1.429
axis + 3.5 cm.	8.579	8.819	7863	1.426

Mean of all observations 1.448, whence it follows that

$$\chi_{64^{\circ}.9\ \mathrm{K.}} = 284.2\ .\ 10^{-6}.$$

Finally for finding the specific susceptibility the density of oxygen was found from the formula 1)

$$\rho = 1.2489 - 0.00481\ (T - 68).$$

From table II we obtain

$$K_{90^{\circ}.1\ \mathrm{K.}} = 275.2\ .\ 10^{-6}$$
$$K_{71^{\circ}.35\ \mathrm{K.}} = 332.8\ .\ 10^{-6}$$
$$K_{64^{\circ}.9\ \mathrm{K.}} = 359.0\ .\ 10^{-6}.$$

Table III gives $\chi\sqrt{T}$ for each of the temperatures and for each of the series.

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1) Baly and Donnan. J. Chem. Soc. 81 (1902) p. 907.

TABLE III.

Series with the first apparatus			Series with the improved apparatus		
T	$\chi \cdot 10^6$	$\chi\sqrt{T} \cdot 10^3$	T	$\chi \cdot 10^6$	$\chi\sqrt{T} \cdot 10^3$
90.1	237.3	2.25	90.1	240.6	2.283
71.35	272.0	2.29	71.35	269.9	2.279
63.9	283.4	2.26	64.9	284.2	2.289
mean		2.27			2.284

There is no systematic change to be noticed in the product $\chi\sqrt{T}$; the greatest deviation from the mean is 1 $^0/_0$ with the first apparatus, and only $^1/_4$ $^0/_0$ with the second; moreover the deviations in the two series at corresponding temperatures are in opposite directions. Hence within the limits of accuracy of the observations the specific susceptibility can be represented by the formula

$$\chi = \frac{2284}{\sqrt{T}} \cdot 10^{-6}.$$

In the comparative measurements which we shall describe in the sequel we shall find the same law, at least as far as its form is regarded. For the discussion of this point we refer to § 5.

The differences between the various values of the ratio $\frac{z}{H^2}$ are greater than we should be led to expect from the accuracy obtained (0.05$^0/_0$) in the measurements with the cathetometer of the displacements of the level, and from the accuracy of the measurements of the field-strengths, of which a discussion is given above. It is certain that the cause of these deviations must arise from a source other than the measurement of these two data, though we cannot with certainty indicate what this may be.

We may in the meantime remark that, at least in the case of the first series, the unsteadiness of the apparatus in the vertical direction in the not quite homogeneous field, and the slight inconstancy of the temperature have certainly been contributory causes of these deviations, since the second apparatus which was improved exclusively in these directions gave much more regular results. This remark, however, does not seem to account sufficiently for certain appreciable changes that occurred without any noticeable corresponding irregularity in the pressure or in the convection current of the liquid, while there was also no noticeable change in the shape of the meniscus.

Liquid oxygen II.

§ 3. *Measurements by the method of the maximum couple exerted upon an ellipsoid.* Further comparative measurements for liquid oxygen at various temperatures were obtained by means of the method of the maximum couple exerted by a uniform field upon an ellipsoid. This method has already been described and discussed in connection with the research on ferro-magnetic substances [1]; it will be sufficient to discuss the modifications which were found to be necessary owing to the particular circumstances under which the method had to be applied to the present research.

In the first place on account of the small value of the susceptibility it was necessary to make the couple to be measured as large as possible; with this end in view we chose an *oblate* ellipsoid of revolution, instead of a prolate; its axis of revolution was placed horizontal in a field which could turn round a vertical axis

The ratio that is taken between the axes is not a matter of indifference; for a given major axis the couple, which is proportional to $(N_1 - N_2)\, v$, is a maximum for a ratio of the major to the minor axis that is only slightly smaller than 3; we have therefore taken this value of the ratio for the construction of the ellipsoids.

We used the same electromagnet as served for the measurements made by Weiss and Kamerlingh Onnes (loc. cit.). Two pairs of pole-pieces were used; first the cylindrical pole-pieces with quite flat end surfaces that had been used for the measurement of the magnetic rise, and then truncated conical pole-pieces the end surfaces of which (slightly concave, see in this connection p. 24) were 4 cm. in diameter, and the side surfaces of which were connected by convex surfaces of revolution to the cylinders that formed the cores; these were 9 cm in diameter. These pole-pieces were constructed to give the strongest possible field when the distance between the poles was taken to be 20 mm. By this means a field of about 16000 gauss was obtained.

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[1] P. Weiss, J. de phys. (4) 6 (1907) p. 655. P. Weiss and H. Kamerlingh Onnes, Comm. No. 114.

Our observations were made with an ellipsoid that was diamagnetic with respect to the surrounding medium — a solid silver ellipsoid immersed in a bath of liquid oxygen. The ellipsoid was turned by the "Société genevoise pour la construction d'instruments de physique" from a block of very pure MERCK silver. A preliminary experiment showed that it was very slightly diamagnetic with respect to air, and that this was quite negligible with respect to the liquid oxygen. The axes were measured microscopically on the dividing engine; this gave

major axis = 1.0973 cm. and axis of revolution = 0.3654 cm.

Furthermore, two intermediate ordinates parallel to the axis of revolution were measured on the dividing engine, and they were found to be 2% greater than the corresponding ordinates of a perfect ellipse with the same axes. This deviation from ellipsoidal shape was confirmed by a direct determination of the volume from the weight and the density, which gave

0.2329 c.c.

while calculation from the dimensions of the axes gave

0.2308 c.c

In the calculations we made use of the value 0.2329.

The cryogenic apparatus, essentially the same as that used by WEISS and KAMERLINGH ONNES is shown in Pl. I fig. 3. Once more we see the *cover* B, the *adjusting tube* f', and the *holder* b'. The cover with its various parts: the cap with the stuffing-box D, glass tube C, window with plane parallel glass plate C_2, the system BG for adjusting the whole apparatus, the tension rods B_4 for supporting the DEWAR tube, the helium thermometer Θ, the little screens to protect the upper portions of the apparatus from cooling, etc. is just the same as before. The DEWAR tube is of the same shape, but the lower portion is of greater diameter. The only difference between the adjusting tube f' and that which was used in the other investigations is that the lower portion f_9' is of greater diameter.

The *holder* and the *torsion spring* are, on the other hand, completely altered. On account of the smallness of the couple to be measured all foreign magnetic actions had to be eliminated as carefully as possible. Preliminary experiments showed us that a metallic holder could not be used, not only on account of the traces of para- or ferro-magnetic impurities that are never absent from workable metals but also on account of the difficulty of keeping the surface sufficiently clean; this difficulty was encountered repeatedly in the silver ellipsoid that we used in our experiments and it is probable that the constant contact of the hands with iron tools plays a part in causing it. Glass seemed to be by far the most suitable material both on account of the absence of inherent magnetization and of the fact that the surface on account of its smoothness can be kept quite clean. The holder which we finally adopted was made completely from glass; it consists of a tube b' 5 mm. in diameter that at b'_3 is drawn out to a narrow but thickwalled stem, 0.7 mm. in diameter. To this stem the silver ellipsoid was attached; for this purpose a hole of sufficient width to fit was bored along one of its greater diameters and the ellipsoid was then fixed at the desired height by means of a little wax that completely filled the narrow space between the glass and the metal. The tube was then pumped free from air and sealed off, so that the liquefaction of the air that it would otherwise contain would be prevented. The flat mirror for measuring the angle of torsion and the oil-damper were also attached to the holder.

The torsion springs. On account of the smallness of the couples to be measured (the constants of the springs were of the order of 1200 c.g.s. while those used for the investigation of the ferromagnetic substances were some ten-thousands) it was found more suitable to use a straight instead of a helical spring. We took a strip of phosphor bronze about 5.5 cm. long (l') and 0.2×0.01 sq. cm. in cross-section. The upper end was soldered to a spiral spring of three turns made from a much thicker strip than the other; the greatest dimension of this strip was horizontal so that in this way it fulfilled its purpose of being elastic to tension while taking no part in torsion; its presence is essential to prevent the breaking of the thin glass stem or of the platinum-iridium stretching wire that is soldered to the stem. This stretching wire is made from a platinum-iridium wire of 0.1 mm. diameter, which was rolled very thin so as to make its torsion constant extremely small without diminishing to any great degree its resistance to breakage. The stretching wire is fused at b'_4 to the lower end of the glass stem, and at its other extremity it carries a knob c' which is held fast in a ring f'_6.

The mounting of the apparatus took place with the same precautions regarding the centring of the whole, the tension of the springs, etc. and by a method similar to that which has been described in the research upon the ferro-magnetic metals.

The course of the observations is very simple once everything has been set up in position. First, those azimuths of the electromagnet are tentatively determined for which the couple in both directions is a maximum. It was sufficient to do these experiments two or three times with suitably chosen field, since the azimuth changes but very little with the field, and for other values of the field one can without danger have recourse to interpolation. After that the series of observations took place in the following manner: Before making a measurement with any particular current this was reversed a certain number of times so as to obtain a well-defined field; we had not here to deal with a value of the saturation-magnetization, which changes but slowly with the field, but in our case the couple was proportional to the square of the field, so that inaccurate values of the field that might be obtained notwithstanding the fact that the iron of the electromagnet was extremely soft would make their influence very strongly felt in our results. Then the electromagnet was adjusted to one of the determined azimuths, the torsion angle was read off for the two directions of the field, the current broken, the electromagnet turned to the opposite azimuth, and so on several times. At the end of a series a measurement with one of the first fields was repeated as a control.

Sources of error, difficulties, corrections, and controls.

1. *Inhomogeneity of the magnetic field.* As will be seen from the following discussion this source of error is by far the most important in our case and is indeed the only one that need be taken into account. If we assume that the field near the centre of the pole-gap may be represented by an expression of the form

$$H = H_0 + \frac{r^2}{2}\left(\frac{\partial^2 H}{\partial x^2}\right)_0 (cos^2 \theta - \tfrac{1}{2} sin^2 \theta) \quad . \quad . \quad . \quad . \quad (3)$$

where H_0 is the field in the centre, and r and θ polar coordinates of a point in the pole-gap with respect to the centre as origin [1]). Let us now replace the ellipsoid by a vertical disc whose diameter is equal to the major axis of the ellipsoid; by taking the expression for the energy of the magnetized disc in the field and differentiating it with respect to the angle between the disc and the lines of force, we obtain for the couple caused by the inhomogeneity of the field:

$$M' = \frac{3}{16} vr^2 I \left(\frac{\partial^2 H}{\partial x^2}\right)_0 sin\,\Phi\, cos\,\Phi \quad . \quad . \quad . \quad . \quad (4)$$

(r = radius of the disc).

The ratio $\frac{M'}{M}$ of this couple for an angle of 45° to the fundamental couple is

$$\frac{M'}{M} = \frac{3}{16} \cdot \frac{\left(\frac{\partial^2 H}{\partial y^2}\right)_0}{(N_1 - N_2) I} \cdot r^2 \,.$$

If then we suppose that the relative change of the field in the space occupied by the ellipsoid is of the order of 1 in 1000, the formula given above shows us that although the disturbing couple a little smaller than the chief couple, the two are *of the same order of magnitude.* Hence we see the great influence that this source of error can have in the investigation of weakly magnetic substances. (With ferro-magnetic bodies it is quite negligible: see the previous paper).

We have accordingly devoted the greatest attention to this source of error. The *conical* pole-pieces were made slightly concave, during which process we every time determined the inhomogeneity of the field by means of a ballistic galvanometer and a small coil that was slightly displaced. We ascertained that the change in the field in a space of about 1 c.c. was certainly less than 1 in 2000. We have not had time to pursue this investigation further, and, besides, we should have to obtain a much more sensitive ballistic galvanometer. But it will be seen that the homogeneity of the field was sufficient for the comparative measurements we proposed to make. We may further remark that all these precautions refer exclusively to the conical pole-pieces; the experiments with the cylindrical pole-pieces were nearly free from these sources of error

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[1]) Cf. P. Weiss and H. Kamerlingh Onnes l.c.

We allow for these disturbing couples in the following way: Assuming that $\left(\frac{\partial^2 H}{\partial x^2}\right)_0 = \lambda H$ the expression for the couple due to inhomogeneity given above becomes ($\phi = 45°$):

$$\frac{3}{32} vr^2 \lambda I H$$

or

$$\frac{3}{32} vr^2 \lambda K H^2,$$

which we shall represent by

$$\beta K H^2.$$

If α is the angle of torsion of the holder and C the constant of the spring, then

$$C\alpha = \frac{v}{2} (N_1 - N_2) K^2 H^2 + \beta K H^2 \quad . \quad . \quad . \quad . \quad (5)$$

Thus just as if there were no correction for inhomogeneity the second side of the equation remains always proportional to the square of the field. Even without knowing that correction, if β is itself a constant we should be able to deduce from the observations whether K is a function of the field or not. We see, however, that the constancy of β requires that of λ, i.e. that the field must remain homothetic no matter how great it should be Now this is not the case as can be seen from the quotients $\frac{2\delta}{H^2}$ in tables V, VII and VIII. Table V shows first an increase, then the quotient reaches a maximum and diminishes considerably; tables VII and VIII show a change in exactly the opposite direction; this is just what one would expect if β were variable and K constant, for the tables refer to two practically identical bodies, of which the one is dia- and the other para-magnetic. Now in either case the fundamental couple (uniform field) is in the same direction while the couple due to inhomogeneity changes sign with the susceptibility; should, therefore the correction in the one case first increase and then decrease, it must in the other case first decrease and then increase. We shall return to this point in § 4.

Since this determination aims only at relative measurements, we have once and for all taken as the value of susceptibility of oxygen at — 183° C the value that was given by the improved apparatus for measuring the magnetic rise. With the help of this value we have calculated the values of β *for each field* from equation (5): (see tables V and VI). These values fall pretty well on a curve. Finally the susceptibility at the lower temperatures is calculated by means of the value of β as a function of the field given by this curve. We shall take the opportunity of the corresponding series of observations to make some remarks upon the influence of the inhomogeneity for each of the three pole-gaps that were used.

2. *The inconstancy of the magnetization as a function of the azimuth.* The general expression for the couple in a uniform field

$$(N_1 - N_2)\ I^2\ v \sin \Phi \cos \Phi$$

only reaches its maximum value just at $\Phi = 45°$, and consequently $\sin \Phi \cos \Phi = {}^1/_2$ since *I remains constant during the torsion.* Here again we see a fundamental difference between the application of this method to the investigation of saturation magnetization and to that of a body of constant susceptibility. It is clear that in the first case the condition $I =$ constant is, as it were, fulfilled by definition. In our case the deviation from this is by no means *a priori* negligible: the two limiting values of I^2 ($\Phi = 0°$ and $\Phi = 90°$) differ in our case by 0.3 %, and since I^2 always changes between these two limits in the same direction the error caused thereby when $\sin \Phi \cos \Phi = {}^1/_2$ is less than 0.1 %.

In contrast with the two foregoing sources of error, the reaction of the magnetized ellipsoid upon the *distribution of magnetism over the surface of the pole-pieces* can clearly have no effect in the case of a body of small susceptibility while on the other hand, it had to be taken into account in the case of the ferromagnetic bodies. Indeed, with oxygen we have to deal with a magnetization that in the strongest fields of the electromagnet reaches a value of only a few units (in the case of iron it was 1700 !).

3. *Influence of the holder.* In this connection we may notice two actions that may go together. In the first place there is the inherent magnetism of the stem, and then there is also an action analogous to that which we wish to measure, for if the stem is not a perfect body of revolution, it is acted upon in the liquid oxygen just as if it were a *supplementary ellipsoid.* We investigated these two sources of error in a blank experiment in liquid oxygen in which the silver ellipsoid was removed, and the surface of the glass was carefully freed from all traces of wax. From this we obtained a maximum of only 1 to $2^0/_{00}$ which need not be taken into account.

4. *The concentration of the oxygen.* The oxygen in the bath contained a little nitrogen, the concentration of which constantly decreased during the experiment owing to its faster vaporization So as to be able to allow for this we analysed the gas at the beginning and at the end of each series of observations. The mean concentration was $1.25^0/_0$ at the beginning and $0.35^0/_0$ at the end (at the moment that the DEWAR vessel was almost empty). We allowed for this concentration as far as possible; in this respect there remains an uncertainty of about $0.3^0/_0$.

5. *Calibration of the suspension springs.* The main torsion spring described above was calibrated outside the apparatus by observing the time of oscillation of a system suspended from it with and without the addition of a known moment of inertia. For the latter we used a bronze ring of rectangular meridian cross section, the diameters and height of which were measured with the cathetometer. Calculation gave the moment of inertia as

$$582.09 \text{ c.g.s.}$$

Care was taken that the spring was subjected to the same tension during the calibration as it experienced while in the apparatus (by attaching suitable weights to it by a torsion-less wire).

For the constant of the spring we found

$$1184.5 \text{ c.g.s.}$$

The platinum-iridium stretching wire gives a torsion couple as well as the spring; the correction for this was determined by the same method as was used in the analogous case by WEISS and KAMERLINGH ONNES (loc. cit.) and it was found to be 0.0152 times the constant of the spring. The difference between the values of the constant at 18° C and at —190° C. is smaller than the errors of observation. The calculations were therefore carried out with the constant

$$1184.5\ (1 + 0.0152) = 1202.5.$$

6. *Oscillations.* The silver ellipsoid should be protected sufficiently from the influence of oscillations arising from external causes by the occurrence of intensive FOUCAULT currents, but the occurrence of these currents, which were unusually strong, gave rise to great difficulties in the observations. In the first place the holder was extremely slow to reach its position of equilibrium. Further, the smallest change in the current flowing through the electromagnet occasioned a sudden kick in the whole moveable apparatus, an immediate result of the oblique position of the ellipsoid with respect to the lines of force. Hence the regulation of the current had to be done with the greatest care. We retained the oil-damper but removed the fixed partitions, for the capillary action of these gave rise to couples that, although small, were still not negligible.

Results of the observations.

TABLE IV*a*.
Cylindrical pole-pieces 21 mm. apart.
$t = -183°.0$ C.

H gauss	Double deflection 2δ cm. of the scale.	$\frac{2\delta}{H^2} \cdot 10^7$	$K \cdot 10^6$
2250	0.37	0.731	277
4537	1.41	0.685	268.8
6676	3.21	0.7200	275.3
8339	5.10	0.7335	278.1
9387	6.44	0.7307	277.5
10120	7.45	0.7274	277.0
10685	8.26	0.7234	276.1
11130	8.99	0.7258	271.6
11440	9.38	0.7167	274.8
11765	9.90	0.7155	274.6

Mean $K_{90°.1\ \mathrm{K.}} = 275.6.$

TABLE IV*b*.
Cylindrical pole-pieces 21 mm. apart.
$t = -201^\circ.1$ C.

H gauss	Double deflection 2δ cm of the scale.	$\frac{2\delta}{H^2} . 10^7$	$K . 10^6$
2250	0.50	0.988	324
4537	2.10	1.020	328.0
6676	4.66	1.041	331.1
8339	7.36	1.058	334.0
9387	9.17	1.042	331.4
10120	10.63	1.038	330.8
10685	11.81	1.034	330.2
11130	12.70	1.025	328.6
11440	13.41	1.024	328.4
11765	14.14	1.022	328.0

Mean $K_{72^\circ.0\ \mathrm{K.}} = 330.0$.

Without correcting for lack of uniformity in the field the means give the following values:

$$\chi_{90^\circ.1\ \mathrm{K}} = \frac{275.6}{1.143} . 10^{-6} = 241.1 . 10^{-6}$$

$$\chi_{72^\circ.0\ \mathrm{K}} = \frac{330.0}{1.230} . 10^{-6} = 268.3 . 10^{-6}.$$

The corresponding results obtained by the method of the magnetic rise were

$240.6 . 10^{-6}$ and $269.3 . 10^{-6}$.

The differences between the results as obtained by the two methods are scarcely 0.4 %. This gives us great confidence in the ellipsoid method even for this particularly difficult determination, and it shows that the method is also suitable for absolute measurements if only the necessary care is taken to ensure the uniformity of the field and the correctness of the shape of the ellipsoid.

We must remember that there was a great number of absolute measurements whose results had to be used (axes and volume of the ellipsoid, constants of the springs, magnetic field, density of the liquid oxygen) and also that the shape of the ellipsoid was not perfect. On the other hand we must remark that the application of the correction for the non-uniformity of the field might conceivably have diminished the correspondence between the results obtained by the two methods. We have, however, both theoretical and experimental grounds for the assumption that this correction remains within the limits of accuracy of not more thad 0.5 °/₀ in the case of cylindrical pole-pieces with flat end surfaces 90 mm. in diameter and at a distance of 21 mm. apart.

TABLE V*a*.
Conical pole-pieces 20 mm. apart.
$t =$ 183°.0 C.
(To determine β we assumed $\chi_{90^\circ.1} = 240.6 . 10^{-6}$.)

H gauss.	Double deflection 2δ cm. of the scale.	$\frac{2\delta}{H^2} \cdot 10^7$	$10^6 \beta$
3685	1.27	0.935	58.5
4615	1.96	0.920	54.7
6944	4.55	0.9437	60.8
9205	7.96	0.9400	59.7
11280	11.90	0.9348	58.5
12835	15.44	0.9374	59.1
14015	18.26	0.9295	57.0
14900	20.19	0.9098	51.9
15585	21.73	0.8945	48.1
16120	22.87	0.8802	44.5

A graph of β as function of H was made, which was used for the following table.

TABLE Vb.
Conical pole-pieces 20 mm. apart.
$t = -208°.2$ C.

H gauss.	Double deflection 2δ cm of the scale.	$\frac{2\delta}{H^2} . 10^7$	$\beta . 10^6$	$K . 10^6$
2296	0.79	1.498	56.0	[357]
4615	2.75	1.291	57.8	[328]
6944	6.82	1.414	58.5	344.2
9205	12.15	1.435	59.8	346.3
11280	18.25	1.434	59 7	346.2
12835	23.67	1.437	59.2	346.9
14015	27.89	1.420	56.5	346.1
14900	30.84	1.389	52.4	345.1
15585	33.24	1.368	48.0	345.0
16120	35.44	1.363	43.8	347.3

The mean with the exception of the two values placed between brackets is 345.9 and it gives

$$\chi_{64°.9\,\mathrm{K.}} = 275.0 \,.\, 10^{-6}$$

while the method of the magnetic rise gave

$$\chi_{64°.9\,\mathrm{K.}} = 283.5 \,.\, 10^{-6}.$$

The difference is 3 $^0/_0$; but in this connection we must remember that the correction for non-uniformity is about 16 $^0/_0$, and that the temperature of the liquid becomes very uncertain at the pressure of 11 mm. under which the liquid boils at this temperature.

Finally, we now give two series of measurements which were made with other pole-gaps so as to obtain other deviations in the uniformity of the field. They were hastily made and under unfavourable circumstances, since oscillations and disturbances caused by the running of machines in the neighbourhood interfered with the observations. We give them more as examples of how the method of calculation followed still leads to good results even when the couples due to non-uniformity of the field are extremely large (28 °/₀ of the chief couple).

TABLE VI*a*.
Conical pole-pieces 18.2 mm. apart.
$t = -183°.0$ C.
(To determine β we assumed $\chi_{90°.1} = 240.6 \,.\, 10^{-6}$.)

H gauss	Double deflection 2δ cm. of the scale	$\frac{2\delta}{H^2} \cdot 10^7$	$\beta \,.\, 10^6$
5013	3 34	1.328	159.2
7547	7.31	1.283	147.4
9993	12.64	1.246	137.9
12165	18.33	1.238	136.2
13760	22.39	1.183	121.7
14900	26.26	1.182	121.5
15750	28.83	1.162	116.6
17005	35.58	1.230	133.9

β was again graphed as a function of H, which led to the correction for K in the following table.

TABLE VI*b*.
Conical pole-pieces 18.2 mm. apart
$t = -208°.2$ C.

H gauss	Double deflection 2δ cm. of the scale	$\frac{2\delta}{H^2} \cdot 10^7$	$\beta \,.\, 10^6$	$K \,.\, 10^6$
5013	46.8	1.861	152	341
7547	10.71	1.880	146.5	348
9993	18.88	1.862	137.5	351
12165	27.92	1 885	130.7	357
13760	35.35	1.868	125.5	359
14900	41 36	1.861	123.0	360
15750	45 67	1.840	122.5	357
17005	51.81	1.791	127.5	347

The mean 353 gives $\varkappa = \frac{K}{1.255} = 279.5.10^{-6}$ a value that is not much smaller than $283.5.10^{-6}$ which was obtained by the method of the magnetic rise.

Solid oxygen.

§ 4. *Ellipsoid of solid oxygen.* In this case observations had to be made directly upon an ellipsoid of oxygen. The oxygen therefore had to be frozen in a mould of approximately the same form and dimensions as the solid silver ellipsoid described above. This new condition necessitated the following experimental arrangement.

The cover and the DEWAR tube are the same as for liquid oxygen, with the exception of the cap D. The adjusting tube is also the same but it is so arranged that it can be moved as a whole up or down, while the whole apparatus remains closed and in its place. With this end in view it is attached to the tube m, which moves through the stuffing-box D''_2; this corresponds to D_2 of the liquid oxygen apparatus, but in this case the wide glass tube C_1 is lengthened by a rigid brass tube M that serves to give sufficient play to the vertical movement of the whole adjusting tube. The former stem k had to be lengthened by the same amount (L''_1 L''_2), and is contained in the tube m.

The holder is also a glass tube b''; it is not however closed, but at b''_3 it changes into a very much narrower tube (0.5 mm.) that ends at b''_1 in a glass ellipsoid a''. To this ellipsoid there is fused a solid stem b''_5 that connects it with the stretching wire. The oxygen gets to the ellipsoid through the holding tube which it enters at b''_6. A rubber tube n (d = 3 mm) admits the gas from outside; it is attached to the inlet tube n_4 that passes through the cover and is soldered to it. With this arrangement it is easy to cause the oxygen to solidify inside the ellipsoid. When the apparatus is ready for use the adjusting tube is pulled upwards by the cap △ till the glass ellipsoid reaches the unsilvered part of the vacuum glass. The vacuum glass is then filled with liquid hydrogen. While the ellipsoid is still connected with a reservoir of oxygen, the adjusting tube with the ellipsoid is slowly pushed downwards until it does not quite touch the liquid hydrogen but is in its vapour. The oxygen is then seen to condense slowly, and, if the operation is carefully performed, the whole ellipsoid and supply tube are seen to fill with liquid oxygen. The tube being lowered still further, vapour is reached that is sufficiently cold to cause the oxygen to solidify. On account of the large contraction of the oxygen on solidification it is seldom that one does not see some empty space in the ellipsoid; the operation must then be repeated several times, since the oxygen that is still liquid at this temperature has a pretty great viscosity and flows with difficulty from the tube; we shall return to this point later. When the ellipsoid is completely filled with solid oxygen the adjusting tube may be lowered right down. A mark is made beforehand, so that the ellipsoid may be accurately adjusted to the centre of the gap when the silvered tube is again in its place

Errors, corrections, auxiliary measurements.

1. *Couples due to inhomogeneity.* As will presently appear, we made measurements not only in liquid hydrogen (solid oxygen), but also keeping everything else the same, at two temperatures in a bath of liquid oxygen (i. e. with the same ellipsoid of liquid oxygen). Since the susceptibility of the liquid oxygen was known, we had therefore two measurements of the couples due to inhomogeneity as a function of the field; they are given in Table VII As a result of the somewhat smaller dimensions of the ellipsoid, these corrections are comparatively much less important.

2. *Purity of the oxygen.* The oxygen was freed from nitrogen by vaporizing a large quantity of impure liquid oxygen under reduced pressure.

3. *Density of the solid oxygen.* We have already mentioned the difficulty of completely filling the ellipsoid with solid oxygen. On account of the opaqueness of the oxygen that has already solidified one cannot with certainty assert that this condition has been fulfilled [1]).

Since the specific susceptibility is determined from a known volume this error would have immediate effect upon the result. We tried to eliminate this error as well as possible by determining the density with the same ellipsoid by filling it with solid oxygen under the same circumstances as those obtaining in the experiments and then measuring the quantity of gas formed from it on vaporization. We may assume that the small cavities that may form are pretty much the same in the various cases. Indeed, from two similar measurements the density measured in this way was found to vary by only about 1%. By taking as the mean density that determined by these experiments, the eventual presence of cavities is allowed for. In this way we obtained

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[1]) When there is an empty space af a few mm^3, however, it can be seen quite well.

$$\rho = 1.41.$$

The *absolute* values of the couples due to inhomogeneity of the field are not modified by a cavity formed in the vertical axis, as was usually the case, for it is clearly those portions towards the surface of the ellipsoid that are the chief contributors to them. On the other hand, they might obtain a greater *relative* influence, but as the observations show, the sum of the corrections arising from this cause is so small that they may be regarded as independent of the susceptibility within the limits of accuracy of the experiments. In that case this difficulty completely disappears.

4 *Dimensions of the ellipsoid.* The internal volume was obtained by filling the ellipsoid with mercury and weighing it. It was 0.1812 c c. The change of volume under atmospheric pressure was found to be of no account by pumping the space above the mercury free from air and observing the position of the mercury in the capillary.

The external axes were measured directly. Then the thickness of the glass at ten different points was determined by focussing a microscope on the image of the outer surface formed on the mercury with which the ellipsoid was filled. It changed but slightly from place to place The mean was taken and twice that value was subtracted from the external measurements. The results were :

1.044 cm.

and

0.335 cm.

Calculating the volume from these figures we get 0.1925 c.c. which is about 6% greater than the true volume as directly determined. This is accounted for by the special shape of the meridian section which curves somewhat too strongly at the outer ends. For calculating the coefficients of demagnetization we took a mean ellipsoid with the same major axis and the minor axis small enough to give the real volume [1]. The data for the calculation were therefore:

1.044 cm.

and

0.3173 cm.

5. *Opposing couple.* The suspension spring and the stretching wire were the same as were used for the liquid oxygen. We must, however, allow for the rubber supply tube for the oxygen. This (which was chosen as thin as possible) modified both the zero and the constants of the total opposing couple, as soon as the pressure difference between the inside and the outside of the tube appreciably altered (on account of the change in shape of the tube). In all our experiments, therefore, we took care that there was a constant pressure difference of 70 mm. between the pressure inside the cover and that inside the holder (the latter was the smaller of the two). We got a very sensitive indication of the constancy of this difference not only from the manometers but also from the zero position of the holder. Experiments carried out outside the apparatus showed that the constant of the total couple changed about 10 % between the complete flattening of the rubber tube by the atmospheric pressure and equality between the pressures on both sides. This corresponds to a deflection on the reading scale of *more than a metre.* If we assume rough proportionality we find that a displacement of 1 cm. would indicate a change in the opposing couple of only 0.1 %. The zero was kept constant to a few millimetres.

The calibration was made under circumstances exactly the same as in the experiments (pressure difference, etc.).

The total constant with the addition of that of the stretching wire was

$$1503 + 18 = 1521 \text{ cgs.}$$

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[1] It is clearly not quite right to do this; there are, however, experimental data to support this method of correcting: V. QUITTNER (Diss. Zürich 1908, also Arch. sc. phys. et nat. Genève, Sept.—Nov. 1908) found that this method of treatment was sufficiently accurate even for discs, bodies that deviate far more from an ellipsoid than those we used.

Results.

TABLE VII.
Calculation of the corrections for non-uniformity from observations made in a bath of liquid nitrogen.
Conical pole-pieces 20 mm. apart.

H	$t = -195°.6$ C.			$t = -210°.0$ C.			$\beta.10^4$ (mean). Double weight given $-195°.6$
gauss	2δ cm.	$\frac{2\delta}{H^2}\,10^7$	$\beta\,.\,10^4$	2δ cm.	$\frac{2\delta}{H^2}\,10^7$	$\beta\,.\,10^4$	
4615	1.18	0.554	—0.137	1.59	0.746	—0.199	—0.158
6944	2.69	5577	127	3.53	0.7322	232	162
9205	4.73	5580	126	6.21	7330	231	160
11280	7,08	5560	132	9.23	7251	250	171
12835	9.17	5564	131	12.10	7341	228	163
14015	11.14	5670	100	14.49	7378	219	140
14900	12.90	5812	060	16.94	7613	162	094
15585	14.29	5884	039	—	—	—	—
16120	15 67	6031	003	20.21	7781	121	040

It can be seen that the values obtained for β are not the same at both temperatures. Meanwhile it has to be applied here only as a correction for the susceptibility of solid oxygen which at the most is 3 %. A difference of temperature of 1° C in the bath under reduced pressure gives more than half the difference between the two values, whence we have given the determination under reduced pressure only half the weight accorded the measurement at ordinary pressure. The uncertainty of the mean has less than 1 % influence upon the value of the susceptibility of solid oxygen. The curve for β as well as its sign correspond with what were found for the silver ellipsoid.

TABLE VIII.

Susceptibility of solid oxygen.
$t = -252^\circ.8$
(bath of liquid hydrogen boiling under atmospheric pressure).

H gauss	2δ cm. of the scale.	$\frac{2\delta}{H^2}\,10^7$	$K\,.\,10^6$ uncorrected.	$K\,.\,10^6$ corrected according to tab. VII.
2296	0.89	1.69	519	533
4615	3.57	1.676	518.3	532.9
6944	7.92	1.642	512.3	527.3
9205	14.07	1.660	515.0	530.1
11280	21.14	1.661	515.2	530.1
12835	27.92	1.684	518.7	532.8
14015	32.96	1.678	517.6	529.0
14900	37.38	1.683	518.4	527.5
15585	40.77	1.678	517.6	523.7
16120	44.05	1.696	520.0	523.6

Mean 529.0

whence it follows that $\chi_{20^\circ.3\,\mathrm{K.}} = \frac{529.0}{1.41}\,10^{-6} = 375.2\,.\,10^{-6}.$

TABLE IX.

Susceptibility of solid oxygen.
$t = -258.9^\circ$
(bath of liquid hydrogen under 70 mm. vapour pressure).

H gauss	2δ cm. of the scale	$\frac{2\delta}{H^2}\,.\,10^7$	$K\,.\,10^6$ uncorrected	$K\,.\,10^6$ corrected
2296	1.19	2.257	600.5	614.5
4615	4.80	2.253	600.1	614.6
6944	10.86	2.252	600.0	615.0
9205	19.24	2.270	602.2	617.1
11280	28.13	2.210	594.3	609.2
12835	37.09	2.250	599.6	613.7
14015	45.05	2.293	604.7	616.7
14900	51.24	2.306	606.8	615.9
15585	55.73	2.293	605.3	611.1
16120	60.20	2.317	608.5	612.1

From the mean 614.0 follows $\chi_{sol.\ 14^{\circ}.2 K.} = \frac{614.0}{1.41} = 435.6 \,.\, 10^{-6}$.

The products into $\sqrt{T}$ are

$-252.^{\circ}8 \qquad 375.2 \,.\, 10^{-6} \sqrt{20.3} = 1690 \,.\, 10^{-6}$

$-258.^{\circ}9 \qquad 435.6 \,.\, 10^{-6} \sqrt{12.4} = 1641 \,.\, 10^{-6}$.

Hence we can represent the two observations pretty well by

$$\chi_{sol.} = \frac{1690}{\sqrt{T}} \,.\, 10^{-6},$$

which is adjusted to the measurement at the higher temperature.

The deviation from this ratio for the lower temperature, however, is somewhat greater than the errors of observation.

§ 5. *Summary and conclusion.* As regards the dependence of specific susceptibility upon temperature our most reliable determination gives

$$\chi_{liq.\ 90^{\circ}.1 K.} = 240.6 \,.\, 10^{-6}.$$

CURIE found $\chi = \frac{33700}{T} \,.\, 10^{-6}$ between 20° C. and 450° C. whence it would follow that for $T = 90^{\circ}.1$ K. $\chi = 374.10^{-6}$, a number that differs essentially from ours ¹).

There is therefore no possibility of extrapolating CURIE's law to the liquid phase of oxygen. This was also the conclusion reached by FLEMING and DEWAR in their first treatment of the question, but after more careful experiments they rejected their former result ²).

The results obtained from the two magnetic rise apparatus at lower temperatures can, within the limits of experimental error,

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¹) R. HENNIG's (1893) result should give

$$\chi = \frac{27600}{T} \, 10^{-6} \text{ and } \chi_{90^{\circ}.\,1 K.} = 307. \; 10^{-6}.$$

²) FLEMING and DEWAR's results: 1st paper (1896) $\chi_{90^{\circ}.1 K.} = 200. \; 10^{-6}$; 2nd paper (1898) $287. \; 10^{-6}$, mean $243.5. \; 10^{-5}$ pretty much the same as our result. According to the mean of the result of FARADAY and BECQUEREL the specific susceptibility for oxygen at 0° is $91. \; 10^{-6}$; this gives by extrapolation from CURIE's law $\chi_{90^{\circ}.\,1 K.} = 299. \; 10^{-6}$. The English savants used this number in their second research for the comparison of the susceptibility of liquid oxygen with that of the gas.

be expressed by a very simple law: *the specific susceptibility is inversely proportional to the square root of the absolute temperature.* From the observations obtained with the more reliable apparatus we deduce the formula

$$\chi_{liq.T} = \frac{2284}{\sqrt{T}} \cdot 10^{-6}$$

which holds to within 0.5 %. None of the results obtained by the method of the maximum couple are in conflict with those deduced from the formula.

The results with solid oxygen approximately follow the relation

$$\chi_{sol.\,T} = \frac{1690}{\sqrt{T}} \cdot 10^{-6}.$$

At the lowest temperatures there is a small deviation indicating a smaller increase at lower temperatures; it is, however, so small that we may still accept the formula given as approximately correct for the solid state of aggregation below the melting point of oxygen and down to 14°.2 K.

Further experiments at more numerous temperatures must show exactly how far these deductions hold for the liquid and solid states. They show (see fig. 5) that there is a jump in the value of χ at the melting point, since

$$\chi_{liq.\,T_m} = \text{amply } 1.3\ \chi_{sol.\,T_m}.$$

We hope to answer the question if this jump really exists by special experiments arranged for the purpose; we may, in the meantime, consider that it does probably exist. What Curie found in the transformation of γ iron to δ iron is analogous to the sudden change which we here assume to exist while the form of the law remains unaltered, and which can occur at the melting point or at a point of transformation to an allotropic modification. Weiss [1]) has shown that this can be accounted for on the assumption that at this particular point di-atomic iron changes into tri-atomic.

On the other hand we consider it probable that the law according to which the specific susceptibility changes with the temperature, viz: inverse proportionality to the square root of the absolute temperature at lower temperatures, gradually transforms into that of inverse proportionality (CURIE's law) at higher temperatures, and that each of these laws, therefore, may be but approximations to the same function over different ranges of values of the independent variable T.

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[1]) P. Weiss, loc. cit.

The supposition that the change of specific susceptibility with density is of no importance lies at the bottom of the assumption of the gradual transformation of CURIE's law into that of $T^{-1/2}$. If, on the other hand, we assume that this change is of importance, that e.g. when the internal pressure is considerable the molecules under its influence undergo not only a compression but also a lessening of their magnetic moments, then a region of great molecular compressibility in which the specific susceptibility should change both with the temperature and with the density should exist between the gaseous phase in which the specific susceptibility would be pretty well independent of the pressure, and the liquid phase at lower temperatures, in which the molecules would not be appreciably affected by an additional external pressure on account of their already great internal pressure, and in which, therefore, the specific susceptibility would also be pretty well independent of the pressure. As regards the difference between the magnetic moment of the elementary magnets in the condition of saturated liquid and vapour and that at normal or smaller density at the same temperatures, it is to be expected according to that representation that this difference will change with temperature in consequence of the change of density with temperature.

The assumption can also be made that complex molecules are formed in the liquid state, and that these diminish the intensity of the elementary magnets; in that case changes in susceptibility of mixtures of liquid oxygen with non-magnetic gases should obey the thermodynamic laws that govern the number of such complexes. But all this must be established by further experiments which we hope to complete; in the meantime the most probable assumption is the old one that the specific susceptibility is independent of the pressure.

As regards the question as to whether the specific susceptibility at lower temperatures still follows the law of inverse proportionality to the root of the absolute temperature, if the ferro-magnetism with a very low-lying CURIE point according to WEISS's theory of corresponding magnetic states does not exist, then the change to a still slower increase with decreasing temperature and the approximation to a limiting value is, perhaps, more probable.

The law of $T^{-1/2}$ at once gives rise to the question if instead of the LANGEVIN elementary magnets whose intensity is independent of the temperature, we should assume that their intensity varies directly as $\sqrt{T}$; that is, that we should assume the existence of elementary currents or electrons moving in their paths with speeds proportional to (and, therefore, determined by) the speeds of molecular heat motions. In other words, while LANGEVIN's theory already supposes that the planes in which the electrons move follow the motions of the molecules, but that the areas described in those planes are still independent of heat motion, we should now assume that the electrons undergo the influence of heat motion at their motion *in* their paths and, if the radius of their path has also become invariable, revolve while remaining in the same position with respect to the atom; they would be electrons that are frozen fast to the atom, an assumption thas has already been made to explain other phenomena.

This addition to LANGEVIN's theory, however, does not lead to a specific susceptibility proportional to $T^{-1/2}$ as one at first sight would be inclined to think, but to a constant specific susceptibility.

To substantiate that addition it will probably be necessary to proceed to still lower temperatures than those of our experiments. It seems at present that it is not impossible that then the law χ proportional to $T^{-1/2}$ changes to $\chi = const.$: our observations on solid oxygen seem to indicate a change in this direction. The assumption to which this is equivalent: viz, that the magnetic motions of the electrons cease at the absolute zero, and to which our experiments seem to lead, is much more satisfactory than that the magnetic motions of the electrons still persevere even at the absolute zero.

The second question to which we devoted attention — the dependence of susceptibility upon field strength — requires no detailed treatment. The method of the magnetic rise seemed in some instances to give a decrease of the order of $1^0/_0$ in a field of 8000 gauss, while the method of the maximum couple gave with the cylindrical pole-pieces up to 12000 gauss only a very small systematic deviation and with the conical pole-pieces (16000 gauss) the deviation was scarcely appreciable.

The solid oxygen ellipsoid with which a much lower temperature was reached seemed to give a small decrease at 16000 gauss; it is possible, however, that a greater deviation is obscured by the correction for the non-uniformity of the field. We consider, however, that, assuming that the experiments were accurate to within 1°/₀ the change of the susceptibility with the field up to 16000 gauss remains within the limits of experimental error. This is in agreement with the theory of LANGEVIN, if this, notwithstanding the deviation from CURIE's law, is still applied.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

No. 117.

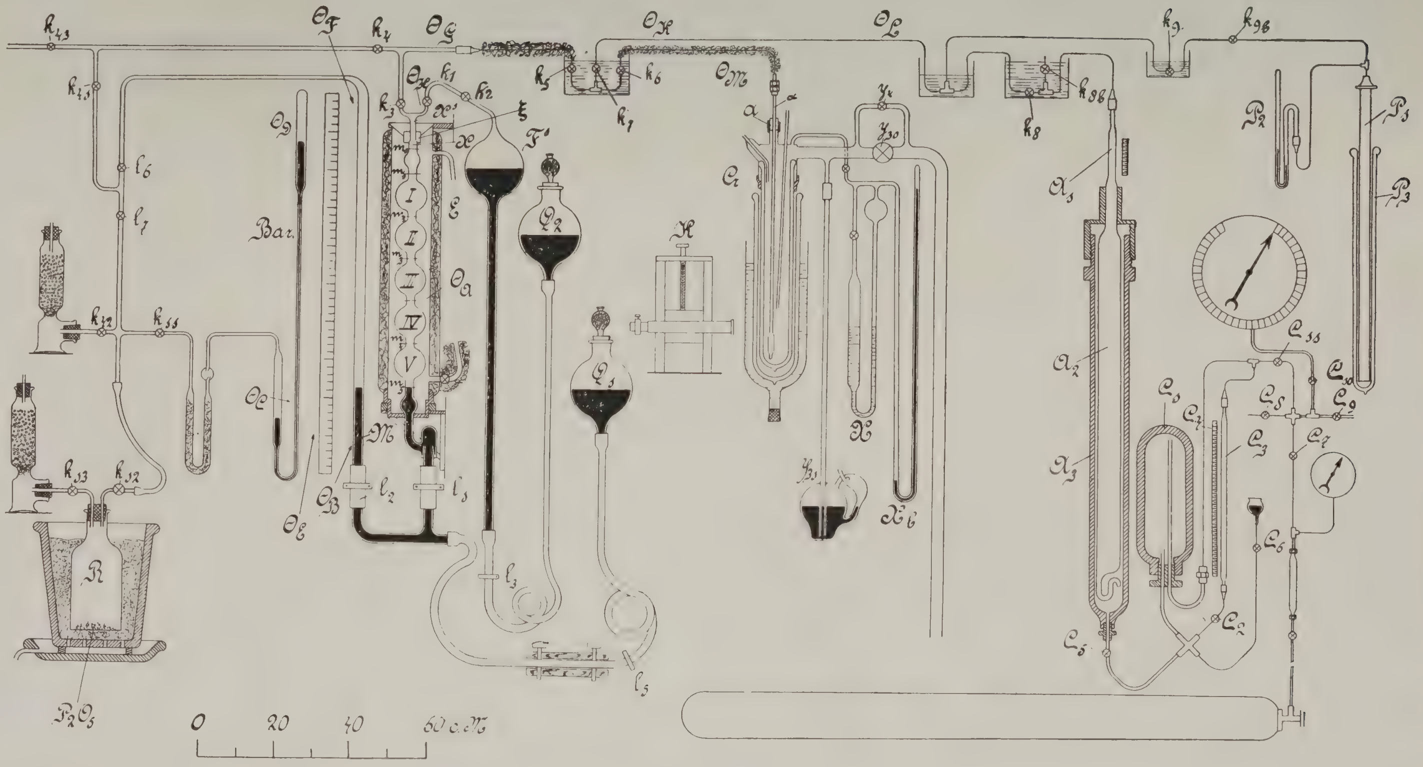
E. MATHIAS and H. KAMERLINGH ONNES. "The Rectilinear diameter for oxygen" (*With three plates*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **28 Januari 1911**, p. 1039—1057).

EDUARD IJDO — PRINTER — LEIDEN.

E. MATHIAS and H. KAMERLINGH ONNES. "The rectilinear diameter for oxygen".

PLATE I.



Communication N°. 117.

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PLATE II.

Fig. 1.

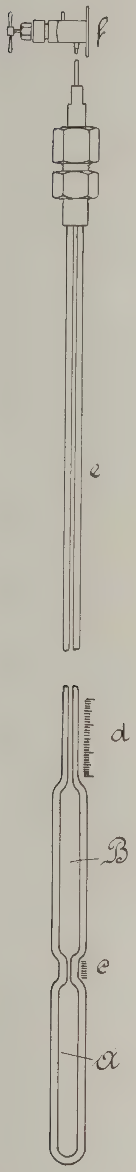

Fig. 2.

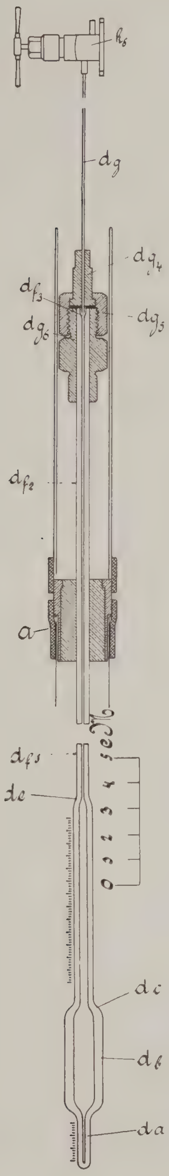

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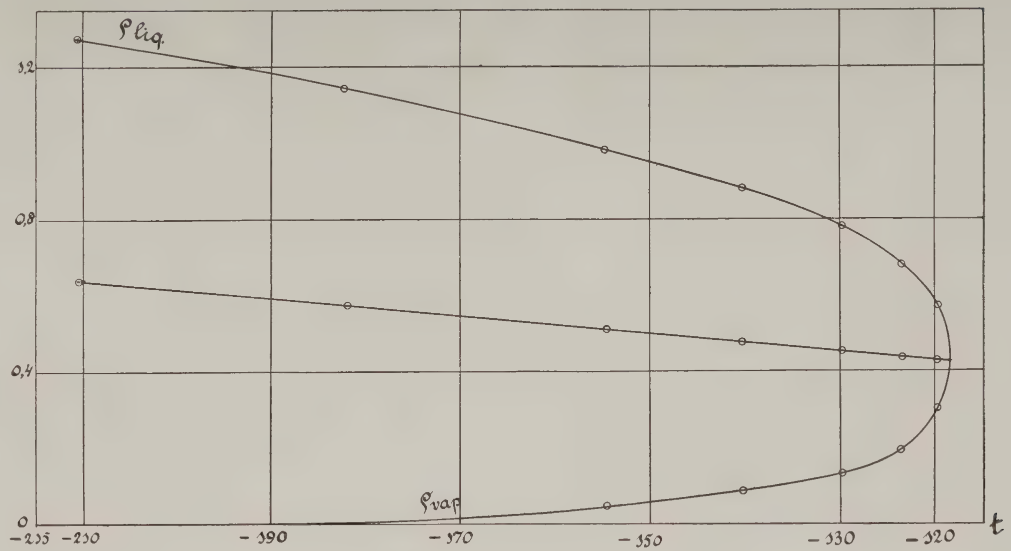
PLATE III.



Communication N°. 117.

E. MATHIAS and H. KAMERLINGH ONNES. "*The rectilinear diameter for oxygen*".

(Communicated to the meeting of June 25, 1910[1]).

§ 1. *Introduction.* As far back as Dec. 1894 the comparison of the equation of state for the permanent gases (particularly that for hydrogen) with the equation for ordinary normal substances was mentioned in Comm. No. 14 dealing with the Leiden cryogenic Laboratory as being one of the first objects for which efforts were made to develop the methods now used for obtaining accurate measurements at very low temperatures. While the law of corresponding states was assumed to be approximately correct for the group of substances of very low critical temperature as well as for other normal substances, there were still reasons for suspecting that their reduced equations of state would show deviations on comparison with those of other substances greater than are found between various groups of ordinary normal substances. In fact, the reduced empirical equation of state for ordinary bodies differs considerably from the original reduced equation of VAN DER WAALS; nor does this difference disappear when the equation is modified by making a calculation of the influence on the kinetic pressure of the finite dimensions of the molecules stricter than that developed by ascribing a constant value to b. At that time the hope could be cherished that substances such as oxygen, nitrogen and hydrogen would, on account of the simpler constitution of their molecules, show a better correspondence with the assumptions upon which VAN DER WAALS based his calculations, and that their reduced equations would approximate to the theoretical VAN DER WAALS equation showing at the same time deviations from the reduced equations for the other substances.

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[1] An excerpt from this paper appeared in the C.R. July and Aug. 1910. The Académie des Sciences at Paris has shown its great interest in the study of the rectilinear diameter of liquids which exist at very low temperatures only, in granting one of us a subvention from the BONAPARTE Fund so as to enable him to come to Leiden. It is an agreeable duty to record our cordial thanks for this.

Operations intended to throw light upon this subject made but slow progress [1]). Cryostats had to be constructed that put a range of sufficiently accurate temperatures at our disposal: the liquefaction of hydrogen soon appeared upon the programme: the piezometry and thermometry of low temperatures had to be studied. In the meantime were discovered the monatomic gases whose molecules probably answer best the assumptions made by VAN DER WAALS, and helium at once usurped the place originally set apart for hydrogen. And now helium itself has been liquefied, but the number of isotherms of different gases that have been determined is small while the region covered by them is narrow. and although the problem that is being worked out at Leiden has undergone important extensions, it still retains the same character as before.

Helium is now the substance to which one would *a priori* ascribe an equation of state most resembling the VAN DER WAALS equation. In this connection it remains to be shown how, from the surfaces which represent the reduced equations of state for ordinary normal substances (passing over first those for oxygen, nitrogen, etc argon, then those for neon and hydrogen) that for helium may be derived by continual deformation; to this one would like to ascribe a limiting form.

Comms. N°. 71 and 74 contain a reduced equation of state obtained by combining the different portions given by various measurements with hydrogen, oxygen, carbon dioxide, ether and isopentane, each for the region of reduced temperature which corresponds with the ordinary temperature for that particular substance. In the Leiden researches this mean equation of state is regarded as an envelope which is in contact with each of the special surfaces of state in that region to which it has contributed to form the mean equation, while the special reduced surfaces for the various substances separate from each other and from the enveloping surface in the other regions, the helium surface in this respect exhibiting the greatest deviations. In fact, the special reduced equation for hydrogen [VII, H_2, Comm. N°. 109*a* § 7 equation (16)] differs markedly from the mean (VII, 1, Suppl. N°. 19, p. 18), and measurements already made with helium (cf. Comm. N°. 108) confirm the fact that its equation of state differs from that for hydrogen in the same way as this has been found to differ from oxygen and nitrogen.

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[1]) See introduction to Comm. No. 97*a* (March 1907).

The deformation of the surface representing the reduced equation of state is accompanied by a deformation of all corresponding lines on it, thus occasioning a change in the reduced values of all magnitudes deduced from the equation. This point will be treated in greater detail in an article by H. KAMERLINGH ONNES and W. H KEESOM on the equation of state and its graphical treatment in the Encyklopädie der Mathematischen Wissenschaften.

One of the most important of these derived magnitudes seems to be the rectilinear diameter. In 1899 [1]) it was shown that the law of corresponding states was not true as regards the diameter for substances as a whole. On the supposition that the diameter is also a straight line for substances of very low critical temperature, the measurements made by DEWAR and by WROBLEWSKI show that for these substances the reduced slope differs greatly from that for ordinary normal substances. This result led to the expectation that the investigation of the diameter would reveal a characteristic feature of the whole representation of the differences between the equations of state for substances of low critical temperature and those for ordinary normal substances, and this the more so as VAN DER WAALS' recent researches upon molecular conglomerations in the liquid state have brought the rectilinear diameter to the front as a means of determining the law governing such conglomerations.

In an investigation of the diameter of substances of low critical temperature the first question encountered is the following It has been shown that for ordinary normal substances the diameter is straight to a high degree of approximation: is this also the case for substances of low critical temperature? Does the deformation of the reduced surface, while occasioning a change in the orientation of the diameter, leave unaltered its rectilinear nature as ought to be the case if this straightness were intimately connected with the innate characteristics of the liquid state? This is the fundamental problem that we have attacked, and is answered in the affirmative by the measurements on oxygen which we publish in the present paper [1]).

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[1]) E. MATHIAS Liège Mém Soc. Roy des Sc 2 (1899)

Oxygen [2]) was very suitable for this first investigation as it remains liquid down to a very low reduced temperature (0.30), and with the cryostat and the thermometric apparatus that had been prepared for the investigation of the isotherms we have mentioned we were able to trace the diameter from the critical point down to — 217° C. (reduced temp. 0.36).

If one were to leave neon and helium out of the question as affording too many difficulties for an investigation of this kind, then liquid densities at still lower temperatures could be obtained with hydrogen only. As yet, however, a cryostat for hydrogen is wanting for temperatures between its boiling point and its critical point, so that measurements for the most important portion of the diameter viz. that part lying between the boiling point and the critical point, are not yet possible, and only that part of the diameter lying below the boiling point, which we may term the produced diameter, is available for measurement.

A final reason for the use of oxygen is that it can be easily prepared in a perfectly pure condition. This was done by heating potassium permanganate contained in tubes forming part of an apparatus made completely from glass. The oxygen liquefied in another part of the apparatus that was immersed in liquid air, and was then distilled from this apparatus into a cylindrical reservoir (see § 4) that was in its turn cooled in liquid air. The quantity of liquid condensed in this reservoir was so regulated that when the ordinary temperature was reached again, the safe pressure allowed by the construction of this copper cylinder was not exceeded.

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[1]) The results were already given in the excerpt published in C R. July—Aug. 1910.

[2]) Measurements of the density of liquid oxygen were announced Comm. N°. 95*b* (1906) pg. 28 note 1.

§ 2 *Method. First Part. The Densimeter.* We deduced the constants for the diameter from measurements of the densities of the liquid and of the vapour at a series of different temperatures. At every density determination for both liquid and vapour the phase whose density was being determined was kept in equilibrium with a small quantity of the coexisting phase.

Fig. 1 Pl. II represents an apparatus with which the diameter can be directly determined. Two equal reservoirs A and B are connected by means of a graduated capillary c; the upper reservoir ends in a narrow capillary coupled to a tap f. The internal volume of the apparatus as far as one of the divisions d is twice the volume of the lower reservoir as far as one of the divisions on the capillary c. The dilatometer is now filled so that at the lowest temperature employed, the liquid meniscus stands at the central mark; the temperature of the apparatus is then raised and each time this is done so much of the vapour is allowed to escape through the tap f that the liquid meniscus always touches the central line. The quantity of oxygen contained in the apparatus at the lowest temperature and the quantities which are successively allowed to escape on proceeding to other temperatures are measured, and corrections are applied for the narrow capillary e, for the difference between the nominally equal volumes V_A and V_B of the two portions A and B and also for the difference between the liquid level and the central mark, and then the data for the diameter are at once deduced from the equation $V_A \rho_{\text{liq}} + V_B \rho_{\text{vap}} = V_A (\rho_{\text{liq}} + \rho_{\text{vap}})$ where V_A is known.

We have not yet used this apparatus, but as we have already mentioned we made use of the less direct method of determining ρ_{liq} and ρ_{vap} separatedly for the same temperature sometimes adding determinations of the difference $\rho_{\text{liq}} - \rho_{\text{vap}}$

To determine ρ_{liq} and ρ_{vap} a glass reservoir of known volume is filled with the phase to be investigated while a small quantity of the coexisting phase is allowed to be present. This reservoir is joined to a narrow glass capillary which allows it to be immersed in a bath of liquefied gas in one of the cryostats of the cryogenic laboratory. The glass capillary is continued by a narrow steel capillary that can be closed by a tap. Since the measurement of the quantities of gas filling the densimeter is, as will be seen in § 3, made in a volumenometer, it would seem desirable to make use of different reservoirs if the densities of the liquid and vapour are to be determined with the same degree of accuracy; but for the purpose of our measurements this was not necessary. To determine a point on the diameter it is not necessary to obtain such a high percentage accuracy in the density of the vapour as in that of the liquid; it is sufficient if the quantity filling the reservoir used for both determinations is known with the same absolute accuracy in each case Hence the same reservoir may be used for determining ρ_{liq} and ρ_{vap}.

As the determination of the vapour density necessitates an accurate knowledge of the volume of the liquid that is left in equilibrium with the vapour, the reservoir of the densimeter terminates at its lower extremity in a graduated appendix a. Unfortunately, the capillary chosen for this appendix was so narrow that in the course of the measurements it was necessary to take the level of the liquid in the conical portion of the capillary above the graduation. In these circumstances it was rather difficult to obtain this correction [1].

The shape of the reservoir was so chosen that the method of constant mass as well as that of constant volume could be employed. With this end in view the reservoir consisted in part of a graduated stem $d_c - d_e$; thus the apparatus formed a dilatometer provided with a very narrow capillary d_f and a tap k_6, as well as an appendix d_a. While the tap k_6 remains closed, the liquid meniscus that at the first temperature stood at the highest mark on the stem which we may call ν_1, sinks as soon as we proceed to lower temperatures. The levels of the liquid $\nu_2, \nu_3 \ldots \nu_n$ corresponding with the constantly decreasing temperatures T_2, $T_3 \ldots T_n$ are read with a cathetometer microscope until at last the level of the liquid sinks beneath the stem $d_c - d_e$ (Pl. II. fig. 2). To turn these measurements to the best advantage, the dimensions of the appendix d_a must be so calculated that when the tap is closed for determinations of the densities of the vapour at the temperatures $T_1, T_2, T_3 \ldots . T_n$ readings of the level $\zeta_1, \zeta_2, \zeta_3 \ldots \zeta_n$ in the capillary of the appendix can be made. In that case one can calculate directly the corrections that must be applied to the rough values of $\rho_{\mathrm{liq}_1}, \rho_{\mathrm{liq}_2} \ldots . \rho_{\mathrm{liq}\,n}$ and $\rho_{\mathrm{vap}_1}, \rho_{\mathrm{vap}_2} \ldots . \rho_{\mathrm{vap}\,n}$ which are obtained by neglecting the correction for the small quantity of the coexisting phase, whereas otherwise these corrections would have to be determined by successive approximations [1]). The condition essential to the successful application of the simple method viz. that accurate equality may be realised between the cryostat temperatures at which the liquid and the vapour densities are determined, was fulfilled in our experiments, and so there was every reason to make use of this circumstance in our application of the method of constant mass to temperatures between T_1 and T_n.

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[1] This was done in the following way: Copies were constructed from pieces of the same kind of glass to exactly the same external dimensions, and of such internal dimensions as to be optically indentical. These copies were then subjected to successive grindings and the internal dimensions were taken after each grinding; the volumes were then determined by integration. We gratefully acknowledge our indebtedness to Mr. G. Holst for the care which he devoted to this part of the investigation.

As determinations of mass in the case of a permanent gas necessitate rather difficult measurements, it can be seen that the number of separate mass determinations necessary when the constant volume method (that in which the dilatometer from a mark on the appendix to the uppermost mark on the stem functions as a densimeter) is exclusively used, ought to be limited to as narrow a temperature range as possible. For this reason the dilatometric method (of constant mass) is combined with the densimetric (or pyknometric) method of constant volume: the former method as indicated above gives the data necesary for a series of intermediate temperatures, while the latter affords, as it were, the standard points in the range of temperatures to be traversed between which intermediate points are inserted to correspond with temperatures occurring between two standard points.

For oxygen, and this is in general the case with the permanent gases, neither the constant mass method nor the constant volume method can be rigorously applied over the whole range of temperatures. To traverse the various regions of temperature it is sometimes necessary to change from one temperature bath to another and this can only happen by exposing the apparatus to the ordinary temperature in between. To do this it is necessary to allow the gas to escape from the dilatometer and then allow it to return when the second low temperature has been etablished. For measurements with oxygen the lowest temperatures are given by a bath of liquid oxygen, from — 217° C. to — 183° C., temperatures between — 183° C. and — 164° C. are obtained with a bath of liquid methane, and temperatures between — 164° C. and — 120° C. with a bath of liquid ethylene. In this way one must begin with a new quantity of material at least three times. Hence some standard points on the temperature scale are given by the nature of the bath itself.

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[1]) E. Mathias. Remarques sur le théorème des états corrsspondants. Ann. de Toulouss 1891.

On the other hand a change of apparatus on proceeding from one region of temperature to another would be a decided advantage from the point of view of obtaining greater accuracy. The expansibility of the liquid and the density of the vapour increase rapidly as the critical temperature is approached: it is clear that if one did not wish to be confined to too small an interval in using the same dilatometer over this region, one would choose varying diameters for the stem and for the appendix. For this reason we constructed a series of dilatometers with different stems and different appendices calculated for a series of temperature intervals. Dilatometers that had to be used at temperatures nearer the critical had appendices and stems of greater diameter than the others. Furthermore, by constructing our dilatometers of two parts united by a graduated capillary we tried to provide ourselves with as many controls as possible, for by this device we should be able to check direct measurements made with each of the individual apparatus with one or more of the measurements that were made with another.

In our first experiments we avoided the complications which we have just described and which are encountered as soon as one attempts to obtain for all the data for the diameter the greatest accuracy possible considering the constancy of the cryostat temperatures and the degree of accuracy with which these can be measured. For this reason we made all our measurements both of vapour density and of liquid density with the same dilatometer whether they were at very low temperature or in the neighbourhood of the critical. Hence this dilatometer was so constructed that it could withstand the critical pressure The great advantage in using a single dilatometer for all the determinations lay in the fact that as soon as it was in its place in the cryostat, one had only to pour in the various liquefied gases necessary for the different baths to be able to traverse the whole range of temperature, and that without having to alter the measuring apparatus in any way during the whole series of determinations. It was also of the highest importance that the densities necessary for the calculation of the diameter should be obtained with the same accuracy over their whole course, while, on the one hand, the largest quantity of gas which we could use for each measurement was limited by the dimensions of the volumenometer, and on the other hand, the accuracy of the measurements at the highest temperature was limited by the degree of constancy of the temperature itself. Moreover, there was no necessity for obtaining a greater degree of accuracy for individual points than that which is possible by this method and which may be represented by a unit in the third decimal place. This accuracy is sufficient to determine if the diameter for oxygen is to be considered as straight, and to deduce its slope with the same accuracy as that with which it has been determined for other substances. In any case this first step was desirable in order that data might be obtained to serve for the calculation of the other apparatus mentioned, and to be useful in leading to a greater degree of accuracy. For the degree of accuracy desired it was seen that it was not necessary to determine vapour densities at the lowest temperatures, for it may be assumed that these densities can be calculated with sufficient accuracy.

The dilatometer is seen in position in the cryostat *Cr* in the diagrammatic plan shown in Plate I, its exact dimensions are given on Plate II, fig. 2. The method of joining the glas capillary d_f to the steel capillary d_g of about 0.6 mm diameter is described in Comm. No. 69, Pl. II fig. 4. The piece d_{f4} is soldered to the glass in the manner described in Comm. No. 27; its end surface is ground perpendicular to the stem; instead of a leather ring steeped in wax a fibre ring was used as packing. This connection as well as all other metal connections and taps are kept under test by immersion in oil — a method introduced in Comm. No. 94*b*; this is done by means of a tube attached at a to the cover of the cryostat in which the dilatometer is placed (see Pl. II fig. 2 and Pl. I).

§ 3. *Method. Second Part. The Volumenometer.* The mass of the gas was determined volumenometrically. We used the accurate volumenometer described in Comm. No. 84. Since then it has undergone some modifications for experiments by KAMERLINGH ONNES and DE HAAS on the compressibilily of hydrogen vapour at and beneath is boiling point the results of which will soon be published. The reservoir for the preparation of mixtures (Comm. No 84, Pl. II, fig. 2) which may be seen in use in the apparatus used for the experiments of Comm. No. 88 and No. 92 was needed neither for our present experiments nor for those on the compressibility of hydrogen vapour The reservoir F' (F of No 84, Pl. II) has a separate mercury holder Q_2 (Pl I) and the capillary connecting this reservoir with the volumenometer is so constructed that the gas contained in it may be driven completely out by the mercury. A second tap k_1 was put in the fork of the tube connecting the volumenometer with the reservoir F'; when gas has been admitted into the volumenometer from the reservoir F' the mercury is allowed to rise above the tap k_2 of the reservoir F' and in the volumenometric determinations the volume of the mercury that has risen in k_1-k_2 is allowed for by reading the position of the mercury from the graduations of the calibrated capillary.

The dead space consists of the portion of the volumenometer that projects above the level (ξ in Pl. I) of the liquid in the bath in which it is placed, and of the spaces between the volumenometer and the taps of the apparatus that are connected with it (for instance, k_4 and k_5 Pl. I) (and usually too, the dilatometer containing that portion of the gas that remained after the greater part had been transferred to the volumenometer), but the great advantage of constructing the reservoir F' in the above way lay in the fact that in the calculation of the masses that are measured, this dead space occurs only at low pressures, so that it is not necessary to determine its temperature so accurately. In fact, nearly all the gas to be measured can be transferred to the reservoir F' which is evacuated beforehand and then filled with mercury, and if the volumenometer is used as if it were a pump there remains to be measured in the dead space only gas that is at a very low pressure. Then, keeping k_3 closed, the volumenometer is evacuated through k_4 and k_{43}, and the gas that has been stored in the reservoir F' is transferred to it; this large quantity is then measured at a temperature that is known with great accuracy.

The connections between the manometer tube M and the large reservoir R in which a pressure is sustained equal to, or if one so desires, slightly different from atmospheric had also undergone some modification for the research on hydrogen vapour compressibilities. Amongst other modifications we may mention that the connections which are to withstand a vacuum are either ground or fused together so that it is possible to measure volumes over the whole volumenometer at all pressures between 0 and somewhat more than one atmosphere. Moreover, a connection may now be made between the upper portion of the manometer tube and the tube of the volumenometer. By this means control measurements are possible when the pressure is the same (and in particular when it is zero) above the mercury in the two portions of the apparatus which then form two communicating vessels for the mercury; in that case, apart from other corrections, the mercury menisci must stand at the same height. Another control consists of determining the barometric height which is read from *Bar* (Pl. I) by producing a vacuum above the mercury in the volumenometer. These controls allow one to judge the accuracy of the data that are necessary for the calculation of the corrections. The uses to which the clips l_1, l_2, l_3, l_5 and the taps k_1, k_2, k_3, k_4, l_6 and l_9 (during part of the observations the latter two were replaced by clips) were put during the volumetric operations and particularly during the control measurements just mentioned need no further description. We may also mention that two pieces of wood were used to compress the rubber tube by being screwed closer together and thus cause the mercury to rise a little so that (following RAYLEIGH's method) menisci that were easily readable could be obtained in the desired position: the clips themselves could also be used for the same purpose. For further details regarding the volumenometer and its working we may refer to the papers already mentioned and also to the forthcoming Communication announced in § 3.

The volumenometer has twice been calibrated below the zero mark, once for the experiments published in Comms. Nos. 92 and 88, and again for the experiments by KAMERLINGH ONNES and DE HAAS on the compressibility of hydrogen vapour. The difference between these two calibrations was less than $^1/_{20000}$. We have allowed for the fact that the temperature of the upper portion of the volumenometer (above the level ξ) differs from that obtaining in the bath surrounding E. For the purpose of the compressibility research the volume of this upper part since Comm N⁰. 92 has undergone some modification, and we have ourselves calibrated the volumes x and x' above the zero mark. We have also used the volumenometer itself to calibrate the dead spaces k_1-k_2, $k_3-k_4-k_5$, and in this, amongst other things, we allowed for the number of times that a tap has been turned on being opened. By the general application of the method we have given of allowing only a low pressure in these spaces a knowledge of their volumes with the accuracy that is attainable by adopting these measures is necessary only in exceptional cases.

The pressure of the gas whose volume is fixed by bringing the mercury meniscus in the volumenometer to one of the marks made for this purpose is given by the difference of level between the mercury in the volumenometer and that in the manometer tube *plus* the barometric height when, as was the case in all our experiments, this manometer tube is in connection with the constant pressure reservoir R. The height of the barometer was given by *Bar.* (For this method see Comm. N⁰. 60 and Comm. N⁰. 84). As a rule the tap k_{13} was opened while equilibrium was being obtained between M and E; it was kept closed while readings were being made. Sometimes, when one wanted better adjustment or readings, advantage was taken of the tap k_{13} to make the pressure in R a few centimeters higher or lower than atmospheric.

§ 4. *Course of the experiments. Auxiliary apparatus.* A tap k_5 connects the volumenometer with a rigidly constructed T-piece which through other taps connects the volumenometer and the dilatometer with each other and with the apparatus in which the oxygen is stored under high pressure; these are a cylindrical reservoir P_1 and an auxiliary compressor A in the glass tube of which marked A_2 the oxygen is contained over mercury. All parts of the apparatus can be evacuated along k_{43}, k_4, k_5 and this is of course always done, and k_{9b} and c_5 kept closed before any oxygen is admitted to the tube A_2 from the reservoir P_1. When, as is almost always the case at very low temperatures, the pressure in the reservoir P_1 is higher than the maximum vapour pressure of oxygen at the temperature of the dilatometer, the oxygen can be simply distilled over into the dilatometer from the reservoir P_1, and by regulating the taps, the liquid can be brought to the desired level in the graduated stem of the dilatometer. The auxiliary compressor is brought into use in making the adjustments when the pressure in the reservoir is lower than that of the liquid oxygen in the dilatometer. The auxiliary compressor, indeed, by closing k_5, k_9 and opening k_8, k_7, k_6 may be coupled to the dilatometer d in Cr to form a piezometer such as is used for the determination of isotherms (see Comms. N⁰. 97*a*, Pl. I and N⁰. 69 Pl. I and II): oxygen is then admitted to the reservoir along k_{9b}, k_9, k_8 and is then transferred to the dilatometer d by forcing mercury into the reservoir by means of compressed air (compare the Plate quoted from Comm. N⁰. 97*a* with that given with the present paper; the letters used are the same in the two cases and their meaning will be found in that Communication); the oxygen is then brought to the desired height in the dilatometer by the admission or removal of oxygen. At the same time one can bring the mercury in A to the graduated part of the stem A_1 by allowing oxygen to return to P_1 if necessary. The auxiliary compressor is evacuated before the admission of mercury; it may also be used in conjunction with a metal manometer previously calibrated with the open manometer of Comm. N⁰. 44 or with the closed manometer of Comm. N⁰. 78 ¹)

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¹) We wish to record our thanks to Dr. C. Dorsman and Mr. G. Holst for the care with which they executed this work.

and with the pressure gauge and scale C (see Pl. I) for reading off the vapour pressure of the liquid oxygen in the dilatometer. This measurement is made while the meniscus is in the middle of the dilatometer reservoir d_b, and care is taken to see that equilibrium, as shown by the stationary condition of the meniscus in A_1 is obtained at the same pressure when there remains but a very small quantity of liquid in the dilatometer; from this it is seen that the temperature is the same over the wole dilatometer, and in particular that it is the same for the appendix and for the middle of the bath where the temperature is measured.

The copper cylindrical reservoir P_1 with the tap k_{9b} is of the type that is commonly used in the cryogenic laboratory; to it is attached a small manometer the pressure on which shows the quantity of gas that is still left in the reservoir. The oxygen that has been used for the measurements can be brought back again by distillation on immersing the reservoir in liquid air. The space between k_9 and k_{9b} is used for taking definite small quantities of gas from P_1.

For a detailed description of the arrangement of the cryostat *Cr* (Pl. I of this Communication with the same letters as in Comm. N⁰. 97*a*) and for particulars regarding the cycle of liquid gas that is used when the bath that is being worked with is liquid oxygen boiling under reduced pressure, we may refer to Plate I of Comm. N⁰. 97*a* and to Comm. N⁰. 94*d*. For the cases in which the temperatures are given by baths of liquid methane and liquid ethylene the apparatus is the same in principle. The place occupied by the piezometer in the researches to which reference has just been made is now taken by the dilatometer *d* Instead of a single resistance thermometer as was used in Comm. N⁰. 94*d* we now used two platinum resistance thermometers [1]) each of them with four leads and of the type constructed wholly of platinum and glass (see Comm. N⁰. 99*b* § 2); the glass cylinder was heated until it was beginning to become slightly soft and then the very fine platinum wire was wound on it while it was still hot, the ends of the platinum wire were fused into the glass and then each of them was welded in the blowpipe to two platinum leads.

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[1]) The resistance thermometers were calibrated and the temperature determinations were made by Mevr. DE HAAS—LORENTZ: we gratefully knowledge the careful assistance she gave us in this.

In the present instance the cryostat vessel was a transparent double-walled vacuum glass. In order to keep the lowest temperature always in the bottom of the cryostat by diminishing the evaporation it was surrounded by a second transparent vacuum glass containing liquid air; the latter was protected from precipitation of mist on its outer surface by another glas filled with alcohol whose temperature was kept above the temperature of the room. (Cf e. g. Comm. N⁰. 108).

When the equilibrium that was wanted for a measurement has been reached and the temperature measured while the equilibrium has been maintained, the tap k_6 is closed, the volumenometer and the dead space evacuated (keeping k_7 closed) and then the gas is removed from the dilatometer to the volumenometer.

The temperature of the volumenometer is kept constant by a stream of water delivered by the thermostat described in Comm. N⁰. 70. Thermometers of the requisite accuracy for each measurement were placed at θ_A in the bath and also at θ_B . . . where they where bound to the tubes etc. and were as far as possible wrapped along with them in one common layer of wool.

The volumenometer, the manometer tube with scale alongside and the two limbs of the barometer *Bar* are so disposed around a three telescope cathetometer (Comm. N⁰. 60) that they can all three be read in succession by simply turning the cathetometer round its axis. To facilitate adjustment the barometer and the scale are placed on small tables (Comm. N⁰. 95*e*) which allow of horizontal motion by screw travels, and which can undergo alteration with respect to the vertical. Electric lamps serve to illuminate small vertically movable screens with slits placed behind the menisci, or, in conjunction with mirrors, to illuminate other points; they are switched on in succession from a dial close to the cathetometer from which place the screens too can be adjusted to the desired height. For particulars as to the precautions adopted during the measurements we refer to the Communications already mentioned.

§ 5. *Calculation of experimental results, corrections.* The dilatometer was calibrated with mercury. For this purpose there was temporarily fused to d_a (Pl. II fig. 2) a small glass tap with a capillary that was immersed in a tray of mercury. The volume of the meniscus was allowed for from the data given in Comm. N°. 67; for most menisci it is sufficient to regard them as segments of a sphere. The expansion of the glass was corrected for from the data of Comm. N°. 95*b*. The positions of the liquid in the dilatometer stem must be corrected for the liquid in the ring shaped meniscus that rises up against the glass; to determine this correction we first got the height by an estimation with the micrometer eyepiece or by a measurement made with the micrometer wire of that eye piece; it is very difficult, however, to fix the base of the meniscus In the end we used the results obtained by graphical calculation of the meniscus from the laws of capillarity [1]).

Finally, to determine the quantity of gas given off by the liquid whose corrected volume we have just found from the mass of the gas in the dilatometer up to the tap k_6, we must make allowance for the mass of gas in the dead spaces of the narrow capillary, of the small portion d_{f3}, and of the steel capillary d_g that connects the glass capillary with the tap k_6.

The temperatures of the various parts of the narrow glass capillary depend upon the level of the liquid in the bath. Taking this into account they were taken from isotherm measurements, particularly from those given in Comm. N°. 97*a*.

The pressures used in the various experiments were always those of the saturated vapour; for the greater part of the measurements they were found in the manner indicated in § 4. For temperatures at which the density of the saturated vapour is sufficiently small to be calculated, vapour pressures were found by interpolation from the measurements just mentioned and from the earlier determinations of Comm. N°. 107*a*.

Seeing that oxygen isotherms have not yet been determined for low temperatures the densities in the various parts of the dead space were obtained by calculation, starting from the mean reduced equation of state VII, 1 (Suppl N°. 19, pp. 17 and 18) given by equation III of Comm. N°. 74 by omitting the terms succeeding $\mathfrak{C}$ and taking account of note 1, Comm. N°. 97*a* p. 24.

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[1]) Mr. DE HAAS was kind enough to undertake this calculation for which we wish to record our thanks to him.

In this we put

$$t_k = -118°.8, \qquad p_k = 50.8$$

$$T = t + 273.09 \quad \mathfrak{B} = \frac{B_A}{T_k^2} p_k \frac{1}{A^2_{A0}}. \qquad \mathfrak{C} = \frac{C_A}{T_k^3} p_k^2 \frac{1}{A_{A0}^3}$$

$$A_{A0} = 1 - (B_{A0} + C_{A0} \, . \, . \, . \, . \, .)$$

in which A_{A0}, B_{A0} . . are the values of A_A, B_A . . . at 0° C,

$$A_A = (1 + \alpha_{AV} t) \, A_{A0}, \qquad \alpha_{AV} = 0.0036618$$

$$p v_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v_A^2} + \, . \, . \, . \, .$$

(Comm. N°. 71) Since the question is one of calculation of density at a given pressure the last equation is transformed to

$$p v_A = A_A + B^{(p)} \, p + C^{(p)} \, p^2 + D^{(p)} \, p^3 + \, . \, . \, .$$

in which

$$B^{(p)} = \frac{B_A}{A_A}, \quad C^{(p)} = \frac{C_A A_A - B_A^2}{A_A^3}, \quad D^{(p)} = \frac{2B_A^3 - 3A_A B_A C_A}{A_A^5}$$

(cf. Comm. N°. 92, II, p. 18 and N°. 109, p. 7).

In exactly the same way densities at ordinary temperatures may be obtained from the isotherms of Comm. N⁰. 78. These do not allow the proper evaluation of C_A in the equation given above; on the other hand as is shown in Comm. N⁰. 71 AMAGAT's isotherms are uncertain as far as B_A is concerned. We therefore take the value of C_A from VII. 1 and subsequently B_A from the isotherms of Comm. N⁰. 78.

From VII. 1 we get

			B_A	C_A
at	0°	C.	$-0.82164 \, . \, 10^{-3}$	$2.1255 \, . \, 10^{-6}$
	15.°6	„	$-0.70050 \, . \, 10^{-3}$	$2.1221 \, . \, 10^{-6}$
	20.°0	„	$-0.66747 \, . \, 10^{-3}$	$2.1238 \, . \, 10^{-6}$

and from the individual isotherms (Comm. N⁰. 71 p. 10):

			B_A	C_A
at	0°	C.	$-0\;9295 \, . \, 10^{-3}$	$2.2931 \, . \, 10^{-6}$
	15.°6	„	$-0.7828 \, . \, 10^{-3}$	$2.1925 \, . \, 10^{-6}$

values which do not differ much from those deduced from VII. 1.

Limiting ourselves to the lowest pressures so that the term in C is at the most 10% of that in B we get from the isotherms of Comm. N°. 78

			B_A
at	0°	C.	$-1.02843 \,.\, 10^{-3}$
	15°.6	„	$-0.86388 \,.\, 10^{-3}$
	20°	„	$-0.87466 \,.\, 18^{-3}$,

and these values are contained in the formula

$$10^3 \,.\, B_A = -1.02843 + 0.008942\, t.$$

$$A_{A_0} = 1.00103.$$

This formula was also used for the calibration of the steel capillary $k_6 - \alpha$ with high pressure oxygen using the auxiliary compressor and the volumenometer

The equation that is necessary for the reduction of the volume of a quantity of gas measured in c.c. in the volumenometer at a certain pressure and temperature to the normal volume N (at 0° C. and 760 mm.) of that quantity expressed in c.c. may also be obtained from the equation for ordinary temperature. One can easily see from the numbers given above that in these circumstances $C^{(p)}$ is negligible, so that

$$\mathrm{N} = \frac{pV}{A_{A_0}(1 + \alpha_{AV}\, t)\,(1 + B^{(p)} p)},$$

for which all the date have been found above. Let us use it to determine the pressure coefficient for oxygen between 0°C. and 20°C. and for a pressure of 1 atm. at 0°C. We get 0.0036746 a number that agrees well with that given by JOLLY [1]).

For the normal density of oxygen we have taken the mean of the values [2]) given by LEDUC, RAYLEIGH, and MORLEY: 0.00142876, 0.00142905, and 0.00142900, viz: 0.00142894.

For the corrections that are applied in the calculation of the volumenometric measurements which give p, V, t we may refer

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[1]) MAKOWER and NOBLE's measurements are doubtful. They give $\alpha = 0.0036655$ for $p = 0$ instead of 0.0036618, a value that is certainly too high.

[2]) DANIEL BERTHELOT, Ztschr. f. Electrochem. 1904 p. 621.

For insertion in vol. X, Nos. **109–120**.

Erratum Communication N^0. 117.

p. 20 line 8 from the top: for „18^{-3}" read „10^{-3}".

to the Communications already quoted N⁰. 84, 88, 92 and to the Communication that we mentioned in § 3 as soon to appear. The accuracy of those measurements is greater than that which we were able to reach with our dilatometer so that the mass data may be taken as certain. As an example we give the following results obtained by each of us measuring the same mass twice:

11 Nov.	1.74448	
12 „	1.74432	
		1.74440
11 „	1.74450	
12 „	1.74449	
		1.74449
		1.74444.

Hence we can be pretty certain of an accuracy of 1 in 4000 in the mass

To get an idea of the accuracy with which equilibrium to which the measured quantity referred was actually realised, after equilibrium had been reached in our experiment on the density of the vapour and the tap k_6 had been closed we altered the temperature of the cryostat slightly until the liquid phase first disappeared and then reappeared in the appendix. We found that a temperature change of $^1/_{50}$ to $^1/_{20}$ of a degree was sufficient to cause the liquid phase to disappear completely. The absolute values of the temperatures are accurate to about $^1/_{20}$th of a degree except in one case (— 210° C.) in which owing to unfavourable circumstances, the accuracy attained was $^1/_5$th of a degree.

§ 6. *Results.* For ρ_{liq} the density of the liquid oxygen, for ρ_{vap} the density of the saturated vapour with which it is in equilibrium at the same temperature, and for $D_\rho = \frac{1}{2}(\rho_{\text{liq}} + \rho_{\text{vap}})$ the ordinate of the diameter we obtained the following values:

t	ρ_{liq}	ρ_{vap}	D_ρ (obs.)	D_ρ (cal)	O—C
— 210.°4 C.	1.2746	0.0001	0.6373	0.6373	0
— 182.0	1.1415	0.0051	0.5733	0.5730	+ 0.0003
— 154 51	0.9758	0 0385	0.5072	0.5107	— 0.0035
— 140.2	0 8742	0.0805	0.4773	0.4783	— 0.0010
— 129.9	0.7781	0.1320	0.4550	0.4550	0.0000
— 123.3	0.6779	0.2022	0.4400	0.4400	0
— 120.4	0.6032	0.2701	0.4366	0.4335	+ 0.0031

The calculated values of the diameter are taken from the equation

$$D_{\rho\,(\text{cal})} = 0.1608 - 0.002265\, t.$$

The results are plotted on Plate III.

By putting t equal to the critical temperature — 118.°8 C. a value $\rho_k = 0.4299$ is found for the critical density. This value compared with the value of ρ_{liq} at — 210° C., is in good agreement with the law of the *third of the density* [1]).

From

$$b_d = -0.002265$$

the absolute value of the slope of the diameter $D_\rho = a_d + b_d\, T$, taking $T_k = 273.1 - 118.8$ the reduced slope is found to be

$$\mathbf{b}_d = \frac{T_k b_d}{\rho_k} = -0.813.$$

The deviation at — 154°.5 C., the density of the vapour being obtained from the mean equation of state (see § 5), is probably due to an error in the experiment; we have been able to trace a probable cause that would afford a complete explanation of its occurrence. As for the temperature — 120°.4 C., it is in the neighbourhood of the critical state and ought not, therefore, to influence our conclusions.

We come, therefore, to the conclusion that the diameter for oxygen is to a high degree of approximation rectilinear. The liquid densities differ very little from the values given by DEWAR's experiments and by those of BALY and DONNAN. It should also be noted that the values we have found for b_{d}, $\mathfrak{b}_{\mathrm{d}}$, and ρ_{k} are almost identical with the values

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[1]) E MATHIAS Remarques sur le Théorème des états correspondants Ann. de Toulouse t. 5, 1891.

$$b_{\mathrm{d}} = -0.002264,\quad \mathfrak{b}_{\mathrm{d}} = -0.800,\quad \rho_{\mathrm{k}} = 0.4387,$$

deduced by one of us (E. M.) from Wroblewski's measurements at low temperatures.

It may be noticed in conclusion that the critical virial quotient was found to be

$$K_4 = \frac{RT_{\mathrm{k}}}{p_{\mathrm{k}} v_{\mathrm{k}}} = 3.346$$

a value that is smaller than those for all normal substances of higher critical temperature (see Kuenen, Zustandsgleichung p. 60) which run from 3.4 to 3.9; hence oxygen approximates more than any of these to the value given by van der Waals's equation of state, 2.67.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

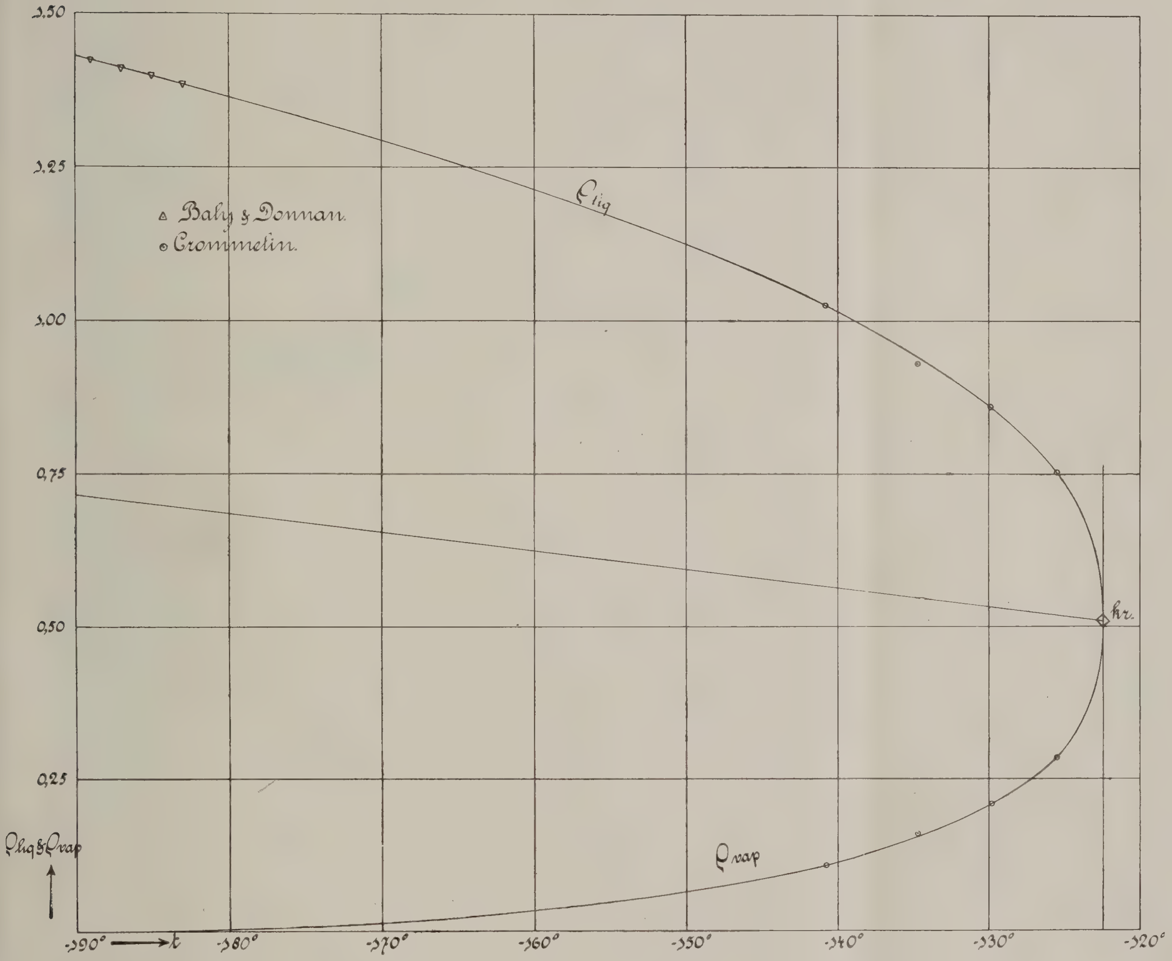
No. 118a.

C. A. CROMMELIN. "Isotherms of monatomic gases and of their binary mixtures. VI. Coexisting liquid and vapour densities of argon; calculation of the critical density of argon". (*With a plate.*)

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **24 Sept. 1910**, p. 390—396).

EDUARD IJDO — PRINTER — LEIDEN.

C. A. CROMMELIN. "Isotherms of monatomic gases and of their binary mixtures. VI. Coexisting liquid and vapour densities of argon; calculation of the critical density of argon".



Communication N°. 118a.

C. A. CROMMELIN. "*Isotherms of monatomic gases and of their binary mixtures.* VI. *Coexisting liquid and vapour densities of argon; calculation of the critical density of argon.*"

§ 1. The experiments published a short time ago [1]) by which the vapour pressures of argon above —140° C. were determined afford a means of deriving the difference between the coexisting liquid and vapour densities at the same temperatures as those at which the vapour pressures were measured. As was mentioned in §§ 2 and 3 of the paper just referred to, both the position of the argon meniscus in the low temperature reservoir and that of the mercury meniscus in the stem of the piezometer (immersed in a water bath at about 20° C.) were read off in the two measurements that formed each vapour pressure determination. As the cross-sections of the reservoir and of the piezometer stem were known and the temperature of the waterbad was noted, and as, moreover, the density of the gaseous argon in the stem could be calculated from argon isotherms which will soon be published by Prof. KAMERLINGH ONNES and myself [2]), all the data necessary for the calculation of the difference between the liquid and vapour densities were known. For the mass of the gas by which the quantity in the stem has been lessened during condensation is equal to the mass of liquid formed *minus* the mass of saturated vapour that at the beginning of condensation occupied the space taken up at the end of condensation by the liquid that has been formed. In the calculation a correction has been made for the volume of the glass stirrer in the low temperature reservoir.

§ 2. The *results* lay no claim to an accuracy equal to that of the vapour pressure determinations in the paper referred to. The accuracy can be estimated at from 1 to $1^1/_2$ %, but the fact that nothing is known concerning the liquid and vapour densities of argon in the region covered by my experiments seemed to me to justify the publication of these results. The calculations (in which, of course, allowance was made for the small impurity in the argon) could be made only for series VI, V, III and IV, and II of Comm. N^0. 115, since the temperature in the two series VIII and IX was in the immediate neighbourhood of the critical temperature, and for these the meniscus was too unsteady to allow of fairly sharp readings.

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[1]) Comm. Phys. Lab. Leiden. N⁰. 115. (1910.)

[2]) Comm. N⁰. 118*b* and C. A. CROMMELIN, Thesis for the doctorate, Leiden 1910.

The results obtained are collected in the following table. As usual the subscripts 1 and 2 refer to the liquid and vapour states respectively; the densities ρ_{liq} and ρ_{vap} are given with respect to water at 4° C.

Date	Series	t	p [1]	$\rho_{\text{liq}}-\rho_{\text{vap}}$
1910. 10 Febr.	VI	−140.80	22.185	0.9195
10 „	V	−134.72	29.264	7718
9 „	III and IV	−129.83	35.846	6502
9 „	II	−125.49	42.457	4714

§ 3. *Deduction of the values of* ρ_{liq} *and* ρ_{vap}. Now that $\rho_{\text{liq}}-\rho_{\text{vap}}$ is known, the values of ρ_{liq} and ρ_{vap} may be reached by assuming that the CAILLETET and MATHIAS [2] law of the rectilinear diameter holds for argon. Considering that the accuracy of the experiments with which we are at present concerned is not very great we may quite well base our calculations on this assumption, the more so as MATHIAS and KAMERLINGH ONNES [3] have just shewn from very accurate measurements that oxygen obeys this law. The applicability of this law to argon, therefore, is not necessarily called into question by the fact that the critical temperature of argon is much lower than is the case with substances for which the validity of the law of the rectilinear diameter has been experimentally established.

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[1] For the sake of completeness vapour pressures (already published in Comm. N^0. 115) are here inserted in the table.

[2] L. CAILLETET and E. MATHIAS. Journ. d. Phys. (2) 5, 549, 1886.

[3] Comm. N^0. 117 and C. R. Ac. d. Sc. Paris 151, 213 and 474, 1910.

To be able to apply this law, however, to our present purpose, we must know the data for the diameter with considerable accuracy. They can be deduced only very inaccurately from the liquid densities given by **Baly** and **Donnan**[1]) which were used along with the diameter in Comm. N^0. 115 for determining the critical density. Their measurements, moreover, cover a range of only 6°, viz. from —189° C. to —183° C., far removed from the critical temperature, and a difference of 0.2 % between the errors in their extreme observations causes an error of about 3 % in the critical density. And further, a small percentage error in the critical density is greatly magnified in the vapour volumes e. g. at —130° C. about 4 times, at —134° C. about 7 times and at —140° C. about 13.5 times. When the values of ρ_{liq} and ρ_{vap} calculated from the estimate of ρ_k (0.496) based on **Baly** and **Donnan**'s results, which was used in Comm. N^0. 115, and the points on the boundary curve deduced from them were accordingly plotted in the *pv*-diagram of the argon isotherms and along with them experimental values of the vapour volumes obtained by slight extrapolation of accurate isotherms, it was seen that they deviated considerably from each other.

I tried therefore to obtain ρ_k independent of **Baly** and **Donnan** with a view to finding the constants of the diameter from it combined with their liquid densities regarded as a determination of $\rho_{\text{liq}} + \rho_{\text{vap}}$ for a single temperature far from the critical. This can be done with the help of the vapour pressures published in Comm. N^0. 115 and of the argon isotherms that are still to be published mentioned in § 1 of the present paper.

At the critical point the equation [2]):

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{dp}{dT}\right)_{\text{coex}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

holds.

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[1]) E. C. C. **Baly** and F. G. **Donnan**, Journ. Chem. Soc. 81, 911, 1902.

[2]) M. **Planck**, Ann. d. Phys. (4) 15, 457, 1882. **Keesom** (Comm. N^0. 75) mentions three proofs communicated to him by Prof. **van der Waals**. One of them can

$\left(\frac{\partial p}{\partial T}\right)_v$ is with great approximation independent of temperature [1]; its values for successive densities in the neighbourhood of the critical density were read from a p, v-graph of accurate isotherms just above the critical temperature. Hence these values hold, too, for the critical temperature itself. The value of $\left(\frac{dp}{dT}\right)_{\text{coex.k}}$ can be deduced from data published a short time ago [2]) viz : $\left(\frac{dp}{dT}\right)_{\text{coex.k}} = 1.820$. Interpolation between the values of $\left(\frac{\partial p}{\partial T}\right)_v$ obtained from the isotherms gave in this way 0.509 as the density for which equation (A) holds.

In connection with the deduction of this value, however, it must be remembered that this method has already led repeatedly to a result for ρ_k differing from that found from the diameter, and that the results obtained by the two methods deviate so far from each other that the difference cannot be attributed to errors of observation or calculation. The values obtained according to these two methods must therefore be regarded as experimental data differing in general from each other and each of them deduced in a certain way. For instance, KEESOM [3]) found 0.00418 for the experimental critical volume of carbon dioxide (expressed in the theoretical normal volume as unit) using the law of the diameter, and 0.00443 for the volume for which equation (A) holds. And KAMERLINGH ONNES and KEESOM [4]) mention that BRINKMAN [5]) found a similar difference in the case of carbon dioxide and of methyl chloride, as MILLS [6]) did for ethyl ether, isopentane and normal pentane. These deviations are such that the

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be found in VAN DER WAALS—KOHNSTAMM, Lehrbuch der Thermodynamik. I, p. 35 and 36.

[1]) Cf. W. H. KEESOM, Comm. N⁰. 88 (1903) (p. 54). Thesis for the doctorate, Amsterdam 1904. p. 86.

[2]) Comm. N⁰. 115, last page.

[3]) l. c.

[4]) Comm. N⁰. 104a, see also Suppl. N⁰. 14

[5]) C. H. BRINKMAN, Thesis for the doctorate. Amsterdam 1904, p. 43.

[6]) MILLS. Journ. of phys. chem. 8. 594 and 635. 1904.

method of the diameter gives the smaller value for the critical volume. It was the deviation between the results obtained by these two methods that led KAMERLINGH ONNES and KEESOM to undertake the study of the disturbance function which must describe the mutual relationship between these and similar deviations. Until it shall appear that this is not the case with argon and it shall be found that the two values agree, as is not impossible for this substance (see below), we must assume that the above value ($\rho_k = 0.509$) is smaller than that which would be given by an application of the diameter law to observations in the neighbourhood of the critical temperature, and this latter value is just the one that we require for our present calculations. In the meantime, however, there is no other course open to us than to base our calculations upon the value just given,

$$\rho_k = 0.509.$$

In this treatment of the question we neglect a difference which, if it could be considered equal to the differences usually existing between values of critical density as determined by these two methods would be much greater than that between the newly derived value and that used in Comm. N⁰. 115 ($\rho_k = 0.496$).

As was mentioned in the beginning of this section (p. 5) a small change in the value of ρ_k is sufficient to cause a large alteration of vapour volume when this quantity is calculated from the law of the diameter, and it is accordingly remarkable that a good agreement is obtained between the observed values and those calculated with the value of ρ_k now deduced. We must ascribe this to the fact that a value of ρ_k happens to have been found which is very suitable for the representation of coexisting liquid and vapour densities by the diameter, and this further leads us to suspect that the two methods of determining the critical density of argon will give results that differ but slightly from each other.

The calculations were made as follows: the diameter was drawn from the observations of BALY and DONNAN in the neighbourhood of the boiling point of argon, the above value of ρ_k, and the critical temperature lately published, — 122°.44 C. From the graph were read values of $^1/_2$ ($\rho_{liq} + \rho_{vap}$) and from these and the observed valves of $\rho_{liq} - \rho_{vap}$, ρ_{liq} and ρ_{vap} were calculated. The results are given in the following table. For the sake of completeness there are also inserted in the table densities d_{A_1} and d_{A_2} in terms of the normal density (the wt. of 1 l. of argon = 1,782 g. under normal conditions according to RAMSAY and TRAVERS [1])) and volumes v_{A_1} and v_{A_2}, in terms of the normal volume; these volumes served along with vapour pressures known from Comm. N^0. 115 for the construction of the boundary curve in the p, v-diagram.

Series	ρ_{liq}	ρ_{vap}	d_{Aliq}	d_{Avap}	v_{Aliq}	v_{Avap}
VI	1.0268	0.1073	576.2	60.21	0.001735	0.01661
V	0.9339	1621	524.1	90.97	1908	1099
III en IV	8581	2079	481.6	116.67	2076	08571
II	7557	2843	424.1	159.54	2358	06268

In the accompanying plate are given curves for the liquid and vapour densities and for the diameter constructed from the above values of ρ_k, ρ_{liq} and ρ_{vap}, the liquid densities given by BALY and DONNAN, and the critical temperature — 122°.44 C. of Comm. N^0. 115.

The unconstrained manner in which the curves could be drawn through the points shewed that in the case of argon there was no necessity to expect any great deviation from the law upon which the calculations were based.

Only the points of Series V (—134°.72 C) do not appear to fit the curve so well, which is no doubt explained by an error of observation.

§ 4. *Representation of the observations by formulae.*

a. The purely empirical formula given by KEESOM [2]) is the most suitable one for this purpose; it may be written in the form

$$\left.\begin{aligned}\frac{\rho_{liq}}{\rho_k} &= 1 + A\,(1-\mathfrak{t}) + B\,(1-\mathfrak{t})^{\lambda}\\ \frac{\rho_{vap}}{\rho_k} &= 1 + A\,(1-\mathfrak{t}) - B\,(1-\mathfrak{t})^{\lambda}\end{aligned}\right\} \quad . \;\; . \;\; . \;\; . \qquad (1)$$

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[1]) W. RAMSAY and M. W. TRAVERS, Proc. R. S. 67, 329. 1900.

[2]) W. H. KEESOM, Comm. N^0. 79. (1902.)

in which A, B, and λ are constants, and t represents reduced temperature.

Bij subtracting these equations the following simple relation is found for the observed magnitude $\rho_{\text{liq}} - \rho_{\text{vap}}$:

$$\rho_{\text{liq}} - \rho_{\text{vap}} = 2\rho_k \, B \, (1 - t)^{\lambda} \, .$$

With the constants

$$\lambda = 0.3795 \text{ and } B = 1.999$$

calculated from the observed values the following correspondence is obtained:

Series	$\rho_{\text{liq}}-\rho_{\text{vap}}$ (O)	$\rho_{\text{liq}}-\rho_{\text{vap}}$ (C)	O—C abs	O—C in %
VI	0.9195	0.9172	+ 0.0023	+ 0.2
V	7718	7874	— 0.0156	— 2.0
III and IV	6502	6493	+ 0.0019	+ 0.3
II	4714	4641	+ 0.0073	+ 1.5

If we calculate the constant A of (1) from the values of ρ_{liq} and ρ_{vap} deduced in § 3, the following correspondence is found for ρ_{liq} and ρ_{vap} as expressed by equation (1) with the value $A = 0.9758$.

Series	ρ_{liq} (O)	ρ_{liq} (C)	O—C abs.	O—C in %	ρ_{vap} (O)	ρ_{vap} (C)	O—C abs.	O—C in %
VI	1.0268	1 0272	—0.0004	0.0	0.1073	0.1119	—0.0046	— 4.2
V	0.9339	0.9424	—0.0085	— 0.9	1621	1566	+0.0055	+ 3.4
III and IV	8581	8574	+0.0007	+ 0.1	2079	2094	—0.0015	— 0.7
II	7557	7506	+0.0051	+ 0.7	2843	2875	—0.0032	— 1.1

The equations therefore give such results as might reasonably be expected from the accuracy of the observations. Slightly better results might be obtained by using least squares. The fact that the deviations of series V are on the whole greater than those of the other series may confirm the suspicion already expressed that an error of observation has been made in that series.

b. Goldhammer's [1]) formula for $\rho_{liq} - \rho_{vap}$ is [2])

$$\rho_{liq} - \rho_{vap} = m\, \rho_k\, (1 - t)^{1/3}.$$

With $m = 3.496$ the following correspondence is obtained :

Series	$\rho_{liq} - \rho_{vap}$ (O)	$\rho_{liq} - \rho_{vap}$ (C)	O—C abs	O—C in %
VI	0.9195	0.8840	+ 0.0355	+ 3.8
V	7718	7731	— 0.0013	— 0.2
III and IV	6502	6526	— 0.0024	— 0.4
II	4714	4859	— 0.0145	— 3.1

The correspondence as might be expected is not nearly so good as that with Keesom's equation.

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[1]) D. A. Goldhammer. Zs. f. phys. Chem. 71. 577. 1910.

[2]) This formula is almost identical with Keesoms's for Keesom gives for pentane 0.3327 as the value of the index which I have called λ. To get as good an agreement as possible, however, I have made an independent calculation of this index for argon.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

No. 118b.

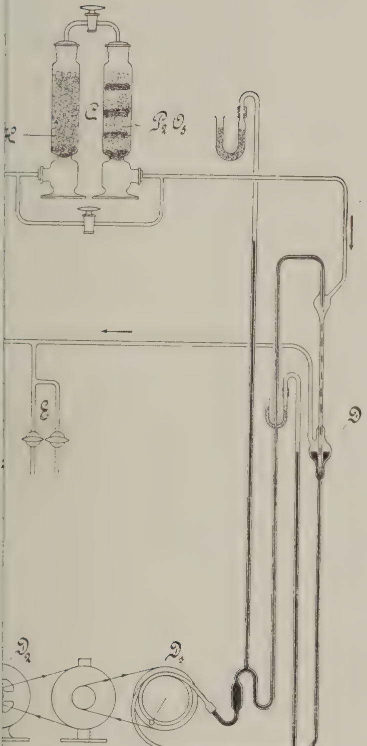
* * *

H. KAMERLINGH ONNES and **C. A. CROMMELIN.** "Isotherms of monatomic gases and of their binary mixtures. VII. Isotherms of argon between + 20° C. and — 150° C." (*With three plates.*)

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **29 Oct. 1910.** p. 582—593).

EDUARD IJDO — PRINTER — LEIDEN.

monatomic gases and of their
C. and – 150° C.”



H. KAMERLINGH ONNES and C. A. CROMMELIN. "Isotherms of monatomic gases and of their binary mixtures. VII. Isotherms of argon between + 20° C. and – 150° C."

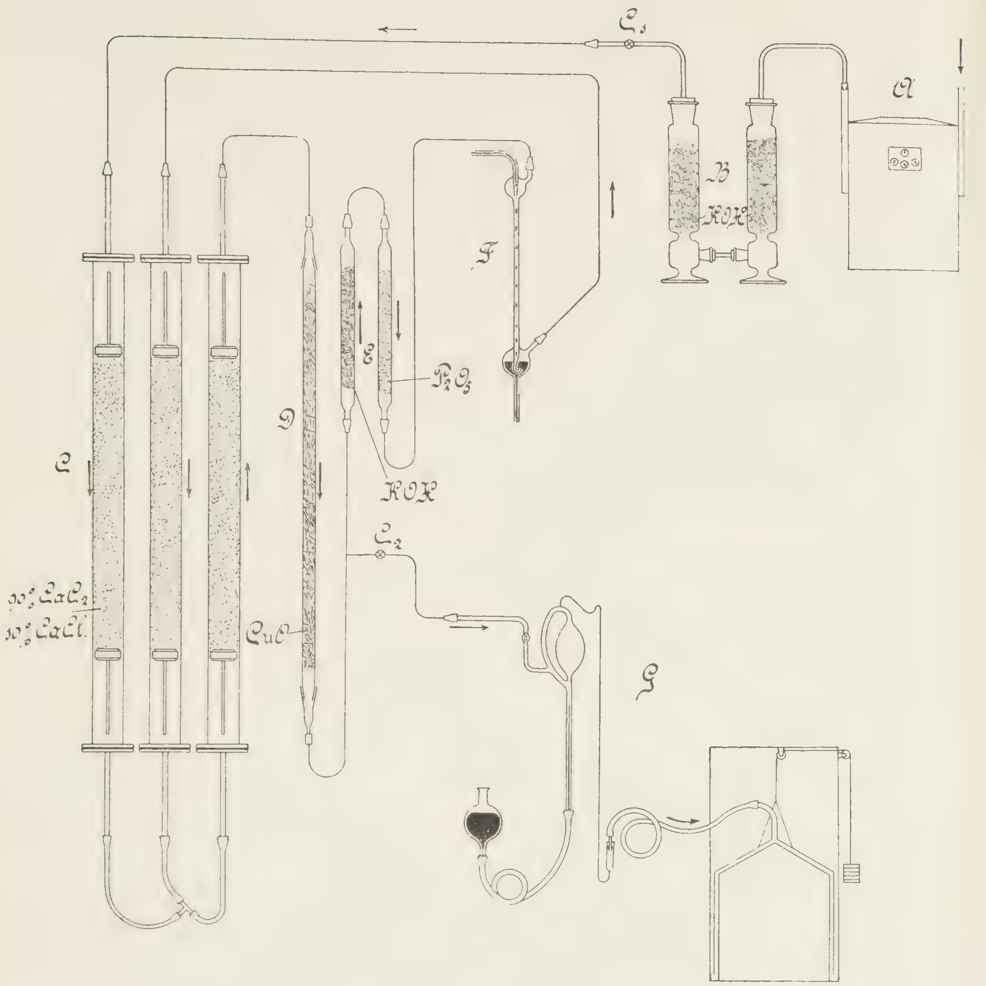


Fig. 1.

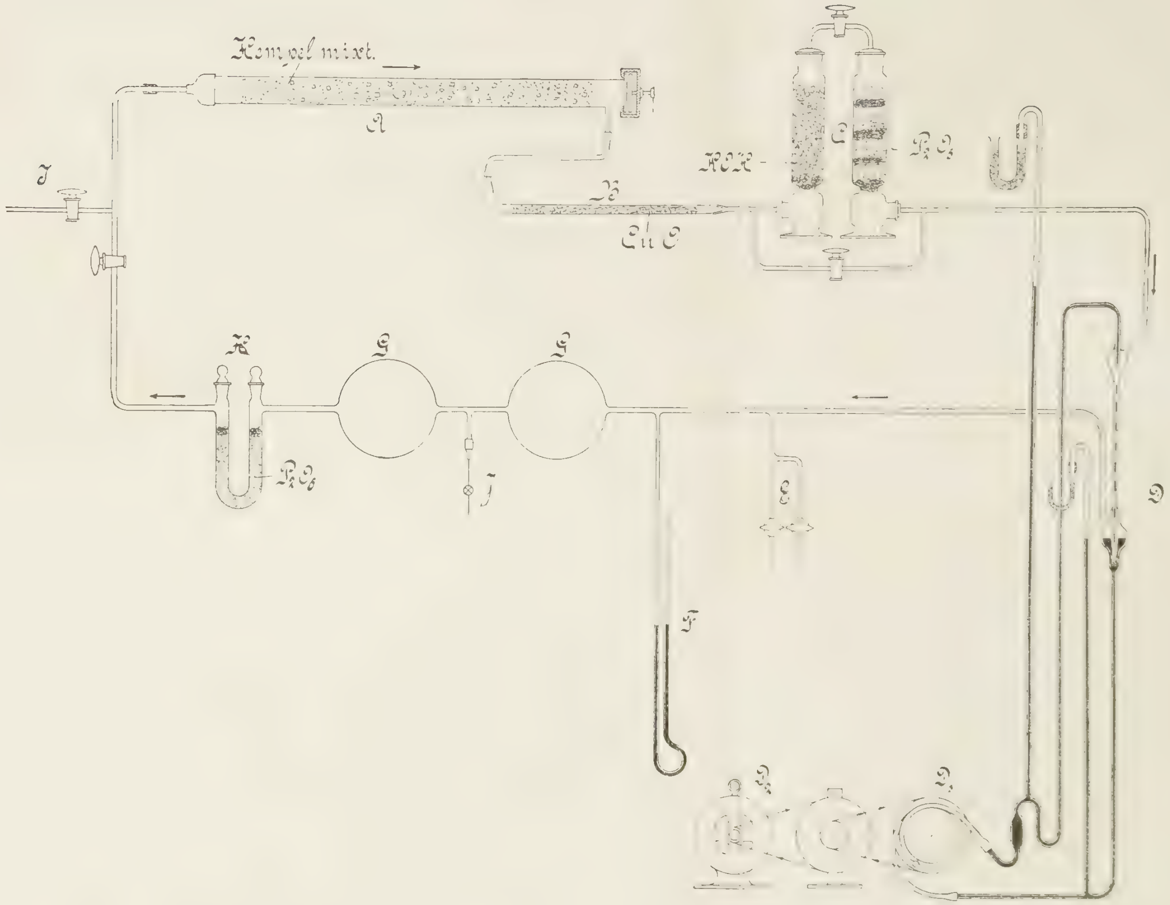


Fig. 2.

Communication N°. 118b

f monatomic gases and of their
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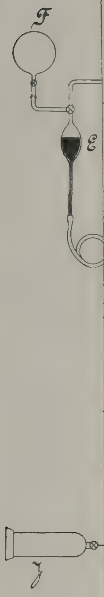

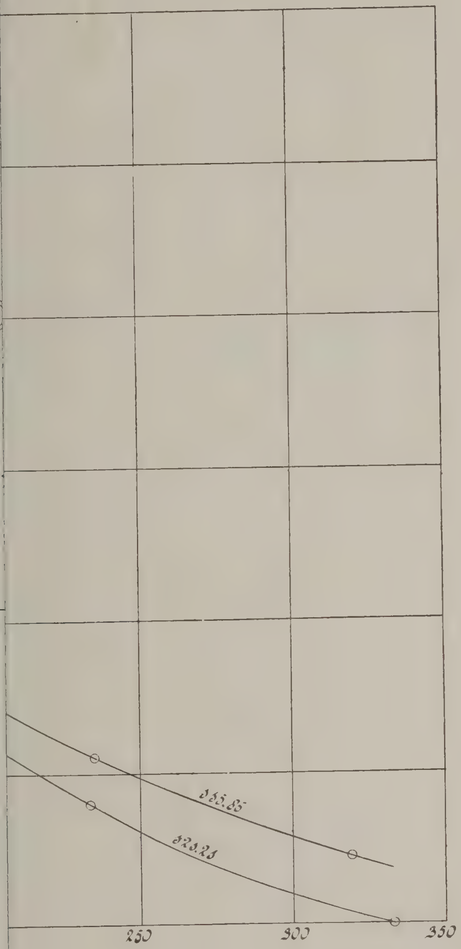

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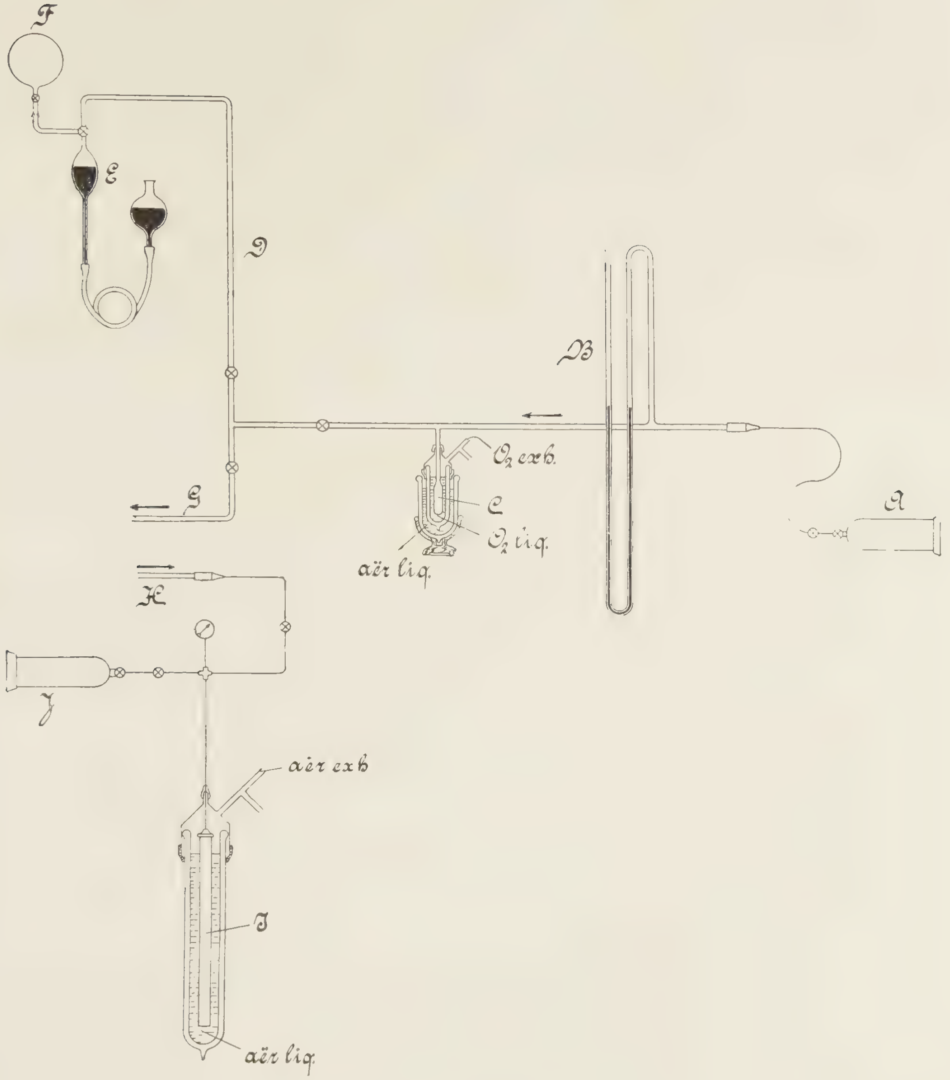


Fig. 3.

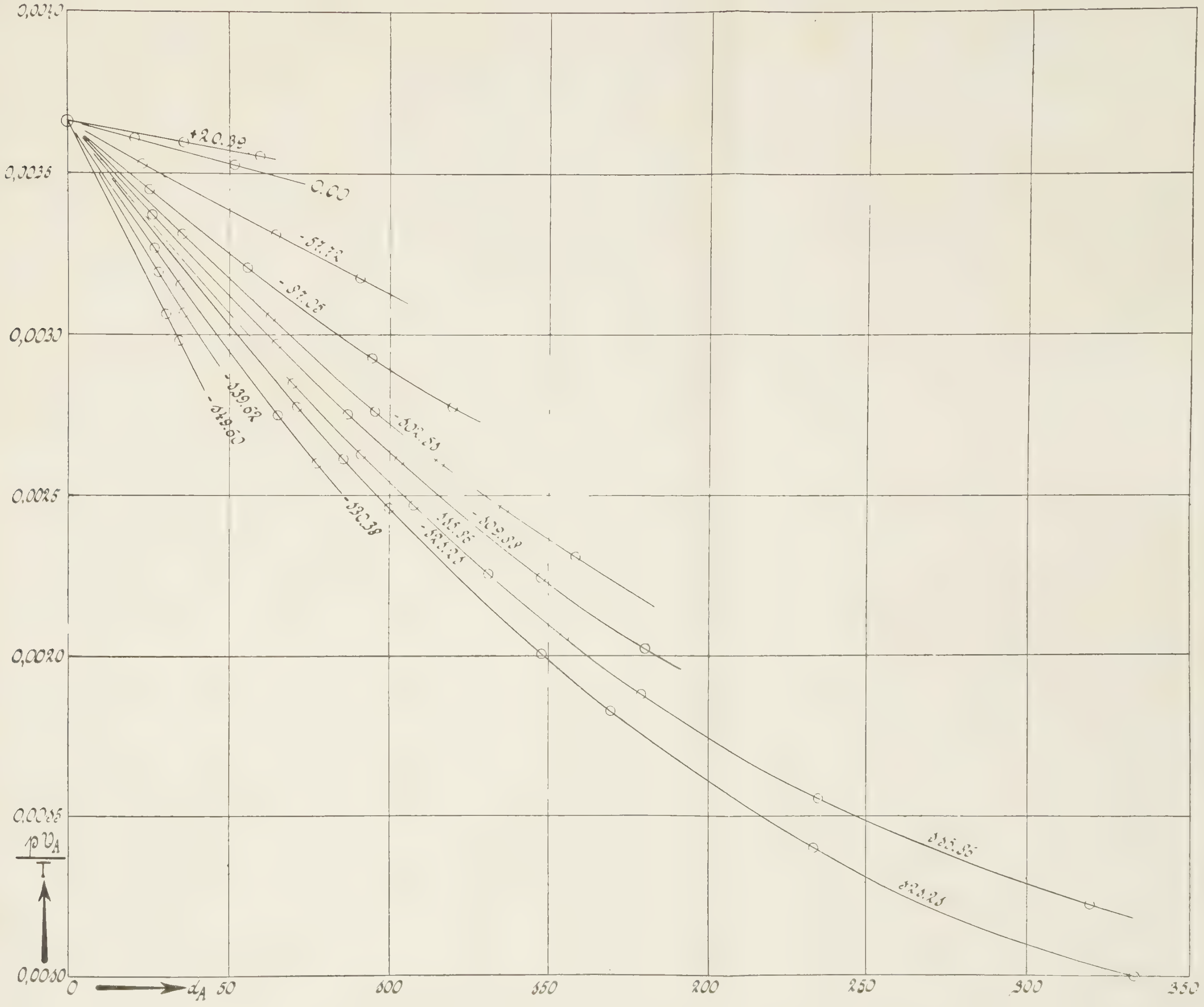
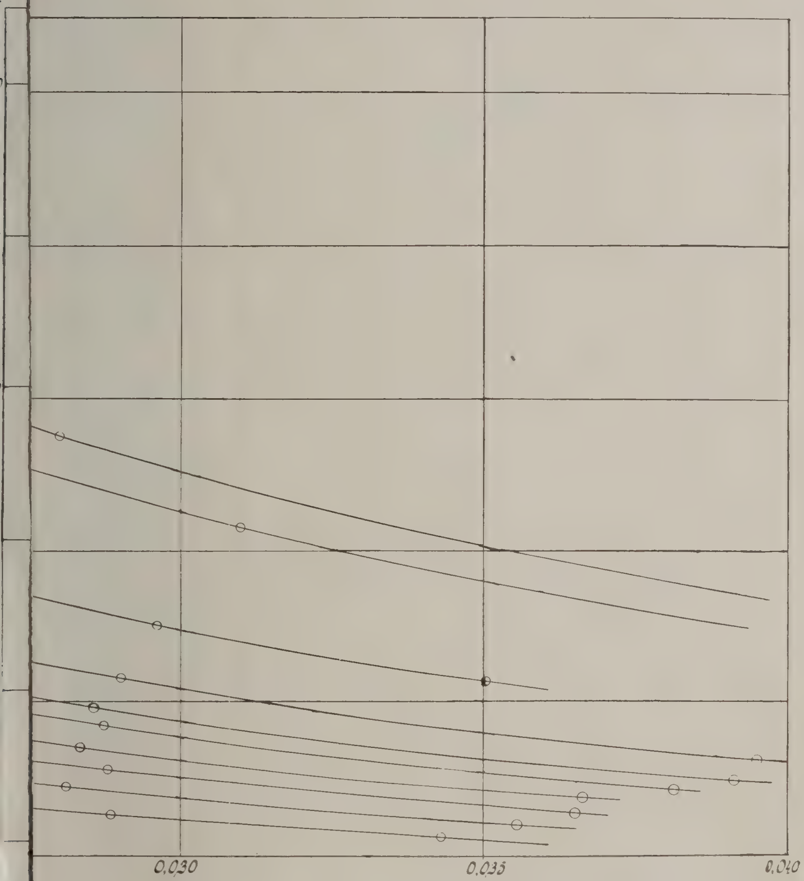


Fig. 4.

Communication N°. 118b.

OMMELIN. "Isotherms of monatomic gases and of their
f argon between + 20° C. and — 150° C."



H. KAMERLINGH ONNES and C. A. CROMMELIN. "Isotherms of monatomic gases and of their binary mixtures. VII. Isotherms of argon between + 20° C. and — 150° C."

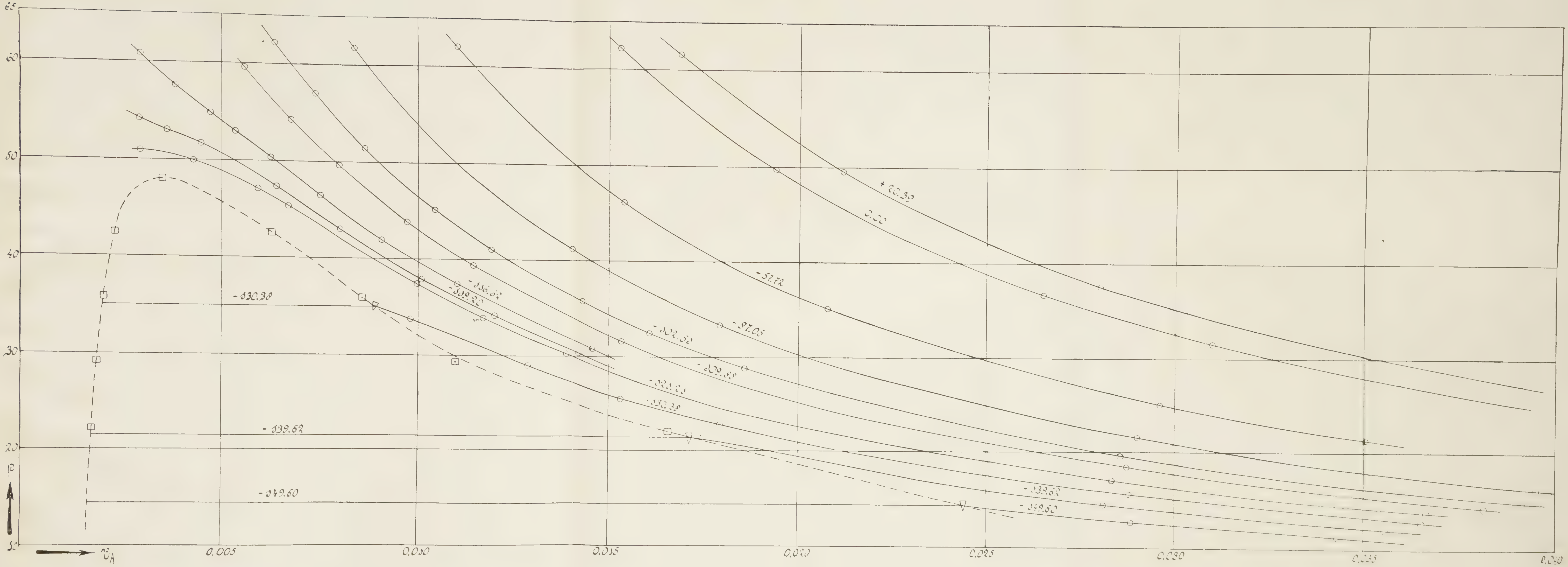


Fig. 5.

Communication No. 118b.

H. KAMERLINGH ONNES and **C. A. CROMMELIN**. "*Isotherms of monatomic gases and of their binary mixtures.* VII. *Isotherms of argon between* + 20° C. *and* — 150° C."

§ 1. In the first publication [1]) of determinations of isotherms of gases at low temperatures made when these had already been a long time in progress mention was made of the desirability of an investigation of argon and helium; to these we may now add neon [2]). We were able to publish helium measurements as early as 1907 [3]), but argon data were not accessible until at a much later period (1909) a sufficient quantity of argon (about 25 L) with not more than 0.1 % impurity was obtained. The method of obtaining this has already been described [4]). This degree of purity is sufficient for isotherm determinations. Measurements of vapour pressures, of critical constants [4]) and also of coexisting liquid and vapour densities [5]) have already been made with the same gas as was used for the isotherms.

As was the case with hydrogen [6]) care was taken in the determination of the argon isotherms given below that the observed points should be appropriately distributed over each isotherm and that suitable temperatures for these should be selected. Still, the shape of the isotherms made it desirable that the points observed should not be so closely packed in normal positions as was the case with hydrogen.

Since all required densities cannot be obtained with one and the same piezometer reservoir, the points for each isotherm must be divided into groups. The various groups of points which afterwards constitute a single isotherm were as far as possible observed at the same temperature by suitable adjustment of the cryostat pressure; corrections given by graphical evalutions of $\frac{\partial(pv_A)}{\partial t}$ were subsequently applied to reduce these to the same temperature. These corrections could not be made with the same degree of certainty as for hydrogen, for then the temperature differences were always less than 0°.2, while differences of fully 0°.4 were experienced in several instances in our present argon measurements.

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[1]) Comm. No. 69 (1901).

[2]) Comm. No. 112 (1909).

[3]) Comm. No. 102 *a*, *b* and *c*, (1907 and 1908).

[4]) Comm. No. 115 (1910) and C. A. Crommelin, Thesis for the doctorate, Leiden, 1910.

[5]) Comm. No. 118*a* (1911).

[6]) Comm. No. 97*a* (1906), 99*a* (1907), and 100 (1907).

In order that the individual coefficients [1]) for each isotherm may be calculated without adjustment from other isotherms, it is of special importance that points observed at temperatures which lie close together should be reduced to the same temperature.

There is yet another circumstance to cause the accuracy of the argon isotherms to be less than that reached in the hydrogen measurements. It has already been shown [2]) that the desired degree of accuracy (from 1 to 0.5 per 1000) cannot be reached with reservoirs of content less than 5 cc. Hence the fact that quite a number of points have been got with a reservoir volume of 2.5 cc. can also account for the smaller degree of accuracy of many points. This table gives for the various series rough values

Series.	Large reservoir.	Small reservoir.
I—XII	600	2.5
XIII—XVIII	2000	5
XIX—XXI	600	2.5
XXII—XXIII	600	5
XXIV—XXXV	600	15
XXXVI—XXXVIII	600	2.5

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[1]) Comm. No. 71. (1901)

[2]) Comm. No. 69 § 6, (1901) and 84. § 19. (1902)

of the volumes in cc. of the large reservoir in the compression chamber and of the small reservoir that is kept at low temperature.

§ 2. The argon used was made according to the methods indicated in §§ 1—3 Part I of Comm. N⁰. 115. For the sake of completeness we now publish some further diagrams of the apparatus used.

Fig 1 [1]) shews the circulating apparatus following that used by Fischer and Ringe [2]).

A, a dry gas meter (air inlet).

B, two potash drying towers.

C, three iron tubes [3]) containing a mixture of 90 % calcium carbide and 10 % calcium chloride, heated in a coke furnace so as to absorb oxygen and nitrogen.

D, a porcelain tube containing copper oxide, and heated in a chemical combustion furnace so as to get rid of hydrocarbons (especially acetylene).

E, two drying tubes containing potash and phosphorus pentoxide.

F, a mercury jet circulating pump (more detailed in Fig. 2).

G, Töpler pump for drawing off the gas that has been treated and an oil gasometer for storing it in.

The cycle working the valves C_1 and C_2 are closed; the gas travels the path indicated by arrows.

Fig. 2. [4]) Apparatus for a working cycle over Hempel mixture.

A, iron tube containing Hempel mixture, and heated in a chemical combustion furnace for absorption of nitrogen.

B, a hard glass tube of copper oxide heated in a small furnace to absorb traces of hydrocarbons that come from the mixture.

C, two drying towers filled with potash and phosphorus pentoxide.

D, circulating pump: a Prytz-pump D_1 worked by an electric motor D_2 raises the mercury. The mercury does not pass through any taps, and the apparatus can be evacuated without allowing any air to force its way in through the pump. The pump can be worked for all pressures in the apparatus less than 1 atm. If the tube of the Prytz-pump breaks the gas in the apparatus can neither escape nor be contaminated.

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[1]) Comm. No. 115, Part I § 1*b*.

[2]) F. Fischer and O. Ringe. Ber. d.d. chem. Ges. 41. 2017. 1908.

[3]) These tubes have already served for the preparation of helium, cf. Comm. No. 108. (1908)

[4]) Comm. No. 115. Part. I § 1c.

E, side tubes for removing and supplying gas.

F, manometer.

G, two vessels each of about 5 L. content, to increase the capacity of the apparatus.

H, phosphorus pentoxide drying tube.

I, a side tube to allow of the removal of the gases developed when the Hempel mixture is heated at the beginning.

J, side tube for the removal of the purified gas, which is then stored in a high pressure cylinder as shown in Fig. 3.

Fig. 3. [1]) Apparatus for the separation of argon and neon by fractional distillation.

A, high pressure cylinder containing argon still contaminated with neon.

B, manometer.

C, reservoir surrounded by liquid oxygen boiling under strongly reduced pressure; in this the argon freezes. A mercury suction pump *E* brings the neon along *D* to the bulb *F*. A Töpler pump then removes the argon along *G*. *H* is the pressure side of this pump, from which the argon at an overpressure of about 1 atm. is passed into the chamber *I*, immersed in liquid air boiling under reduced pressure. When that chamber is filled with solid argon, it is warmed, and the gas blows off to the pure gas storage cylinder *J*.

§ 3. For description of the *apparatus* used for determination of the normal volume and the individual isotherms we may refer to earlier publications [2]) In one respect we introduced an improvement for we took our readings through a telescope with a micrometer eye piece; in this way they could be made at twice the rate possible when using the nonius of the cathetometer. Pressure and temperature readings were made in exactly the same manner as before in determinations of vapour pressures etc. [3]), and the remarks made in the communication of those results apply equally well here. Measurements of pressures below 20 atm. were made with the standard open manometer [1]).

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[1]) Comm. No. 115. Part I § 3.

[2]) Comm. No. 69 (1901), 78 (1902), 94*f* (1906), and 97*a* (1906).

[3]) Comm. No. 115.

We gratefully acknowledge our indebtedness to Miss G. L. LORENTZ and Mr. W. J. DE HAAS for their measurements and calculation of the temperatures, and also to Dr. C. DORSMAN Jr., and Mr. G. HOLST for their measurements with the open manometer.

§ 4. As regards the calculations themselves we may also refer to earlier communications [2]) for there is not much fresh to be said about them. First, isotherms for + 20° C. and 0° C. were calculated using the expansion coefficients for oxygen taken from an earlier paper [3]); the critical constants for argon and oxygen differ but slightly from each other Then the coefficients of the empirical equation of state [4]) A_{A} and B_{A} were calculated to a first approximation, and using the critical constants [5]) a value for C_{A} was got from the set of reduced coefficients VII. 1 [6]). From the equation to which the operations led the expansion coefficients for various densities were calculated, and with these values the calculation of the isotherms was repeated. From these new isotherms to a second approximation, the coefficients were recalculated to a second approximation. For our present purpose a third approximation was found to be unnecessary.

The expansion coefficients at low temperatures which were necessary for the much smaller corrections for the portion of the glass capillary inside the cryostat were at first deduced from AMAGAT's [7]) oxygen isotherms with the aid of the law of corresponding states. Subsequently, when we could avail ourselves of a portion of our experimental data, the expansion coefficients or rather the densities which are in this case easier to manipulate were graphically determined. The degree of accuracy afforded by this method was found to be quite sufficient for our purpose. The second approximations were found to be sufficient for all the isotherms.

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[1]) Comm. No. 44. (1898)

[2]) Comm. No. 78, (1902) and 97*a* (1906).

[3]) Comm. No. 78.

[4]) Comm. No. 71 (1901).

[5]) Comm. No. 115.

[6]) Suppl. No. 19 (May 1908) p. 18.

[7]) E. H. AMAGAT. Ann. d. Chim. et d. phys. (6) 29, June and Aug. 1893.

In the calculations we have made no use of the RAMSAY and TRAVERS [1]) isotherm at + 11°.2 C., for their observations shewed such marked deviations from ours that we could place no reliance upon them.

§ 5. The *results* are contained in the following tables. In the first column is given the date, in the second the series, and in the third the number of the observation; in the fourth is given the temperature in KELVIN degrees [2]) — 273°.09; the fifth and sixth contain the pressure in atmospheres (p) and the density in terms of the normal density respectively, the seventh gives the product of p into the volume expressed in terms of the normal volume pv_A and finally the eighth contains the values of v_A.

Such observations as were for any reason deemed less accurate than the others are placed between square brackets.

Observations marked by an asterisk were made by way of control after the measurements proper were completed because uncertain indications of one of the metal manometers made us for a moment suspect that something had happened to the pressure measurement. The table of deviations given in a subsequent section shows that this fear was baseless.

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[1]) W. RAMSAY and M. W. TRAVERS. Phil. Trans. (A) 197, 47, 1901.

[2]) Comm. No. 101*b*. (1907)

Isotherms of argon. TABLE I*a*.

Date.	Series.	N°.	t	p	d_A	pv_A	v_A
May 11, 1910	XXXV	1	+20°.39	21.783	20.499	1.0627	0.048783
,, ,,	XXXV	2		27.320	25.759	606	38821
,, ,,	XXXV	3		34.487	32.590	582	30684
July 2, ,,	XXXVIII	1		*37.248	35.330	543	28305
Dec. 23, 1909	X	1		37.673	35.759	535	27965
,, ,,	X	2		49.604	47.319	483	21134
July 2, 1910	XXXVIII	2		*61.697	59.134	434	16911
Dec. 23, 1909	X	3		61.741	59.250	420	16878
Dec. 23, 1909	IX	1	+18°.39	37.264	35.401	1.0526	0.028248
,, ,,	IX	2		49.586	47.355	471	21117
,, ,,	IX	3		62.489	60.060	405	16650
May 11, 1910	XXXIV	1	0°.00	20.576	20.877	0.98560	0.047900
,, ,,	XXXIV	2		26.070	26.581	98077	37621
,, ,,	XXXIV	3		31.572	32.302	97740	30958
Dec. 22, 1909	VIII	1		36.743	37.782	97250	26468
,, ,,	VIII	2		49.871	51.840	96201	19290
,, ,,	VIII	3		62.230	65.325	95261	15308
May 10, 1910	XXXII	1	−57°.72	17.872	23.509	0.76023	0.042537
,, ,,	XXXII	2		[21.488	28.575	75200	34996]
,, ,,	XXXII	3		25.228	33.793	74654	29592
Dec. 20, 1909	VI	1		35.127	48.116	73004	20783
,, ,,	VI	2		46.209	64.948	71148	15397
,, ,,	VI	3		62.079	90.695	68448	11026
May 10, 1910	XXXIII	1	−87°.05	16.178	25.152	0.64320	0.039758
,, ,,	XXXIII	2		21.651	34.467	62816	29013
Dec. 21, 1909	VII	1		33.296	55.822	59646	17914
,, ,,	VII	2		41.094	71.444	57519	13997
,, ,,	VII	3		51.533	94.625	54460	10568
,, ,,	VII	4		61.830	119.84	51594	0.0083446

Isotherms of argon. TABLE 1*b*.

Date.	Series.	No.	t	p	d_A	pv_A	v_A
May 6, 1910	XXXI	1	—102°.51	14.864	25.571	0.58130	0.039107
,, ,,	XXXI	2		19.790	35.077	56420	28509
Apr. 6, ,,	XXII	1		[26.143	47.893	54587	20880]
,, ,,	XXII	2		[28.840	53.752	53654	18604]
Dec. 14, 1909	I	1		32.394	62.240	52047	16067
Apr. 6, 1910	XXII	3		[35.784	69.954	51153	14295]
Dec. 14, 1909	I	2		40.976	84.002	48780	11904
,, ,,	I	3		45.088	95.802	47063	10438
,, ,,	I	4		51.398	115.88	44354	0.0086296
,, ,,	I	5		56.882	135.65	41935	73722
,, ,,	I	6		62.239	158.01	39388	63286
May 6, 1910	XXX	1	—109°.88	14.443	26.242	0.55039	0.038107
,, ,,	XXX	2		18.653	34.807	53589	28730
Dec. 18, 1909	V	1		31.515	65.142	48379	15351
July 1, 1910	XXXVII	1		*31.929	66.530	47993	15031
Dec. 18, 1909	V	2		39.166	87.176	44927	11471
,, ,,	V	3		43.718	102.76	42544	0.0097315
,, ,,	V	4		49.515	125.56	39435	79642
,, ,,	V	5		54.250	148.32	36577	67424
July 1, 1910	XXXVII	2		*54.859	152.79	35929	65451
Dec. 18, 1909	V	6		59.616	180.84	32966	55298
Dec. 17, 1909	IV	1	—113°.80	31.001	67.078	0.46216	0.014908
,, ,,	IV	2		38.005	88.889	42756	11250
,, ,,	IV	3		42.682	106.68	40010	0.0093741
,, ,,	V	4		47.655	129.17	36894	77420
March 4, 1910	IV	1		51.752	152.71	33889	65483
Dec. 17, 1909	IX	5		52.188	155.40	33583	64350
March 4, 1910	XV	2		55.763	182.13	30617	54905
Dec. 17, 1909	IV	6		55.991	184.82	30295	54107
March 4, 1910	XV	3		58.898	212.99	27653	46950

Isotherms of argon. TABLE I*c*.

Date.	Series.	No.	t	p	d_A	pv_A	v_A
Dec. 15, 1909	II	1	−115°.86	31.323	69.947	0.44781	0.014296
,, ,,	II	2		37.788	91.308	41385	10952
,, ,,	II	3		41.908	108.02	38796	0.0092574
,, ,,	II	4		46.648	131.51	35469	76037
,, ,,	II	5		50 324	155.12	32442	64464
March 2,1910	XIV	1		53.204	179.94	29568	55575
Dec. 15, 1909	II	6		[54.865	183.35	29923	54539]
March 2,1910	XIV	2		57.493	235.47	24416	42468
,, ,,	XIV	3		61.626	319.52	19287	31297
May 4, 1910	XXVIII	1	−116°.62	13.863	26.480	0.52353	0.037765
,, ,,	XXVIII	2		17.697	34.939	50650	28621
Dec. 16, 1909	III	1		30.681	68.630	44705	14571
,, ,,	III	2		37.250	90.563	41131	11042
,, ,,	III	3		41.943	110.19	38063	0.0090749
,, ,,	III	4		46.496	133.69	34779	74800
,, ,,	III	5		50.259	159.71	31468	62612
March 2,1910	XIII	1		50.447	161.75	31189	61824
Dec 16, 1909	III	6		[53.059	186.15	28503	53719]
March 2,1910	XIII	2		54.922	210.02	26151	47615
,, ,,	XIII	3		[57.617	260.61	22108	38371]
,, ,,	XIII	4		60.669	331.29	18313	30185
May 6. 1910	XXIX	1	− 119°.20	13.766	26.871	0.51230	0.037215
,, ,,	XXIX	2		17.378	34.965	49700	28600
Jan. 7, ,,	XI	1		[30.376	70.314	43200	14222]
March 16, ,,	XIX	1		30.303	70.481	42994	14188
July 1, ,,	XXXVI	1		*30.365	70.580	43021	14168
March 16, ,,	XIX	2		34.052	83.257	40900	12011
Jan. 7, ,,	XI	2		37.641	96.834	38872	10327
March 16, ,,	XIX	3		37.923	98.863	38359	10115
,, ,,	XIX	4		43.006	124.97	34414	0.0080022
Jan 7, ,,	XI	3		[46.082	143.71	32065	69583]
March 16, ,,	XIX	5		47.272	156.36	30233	63955
March 4, ,,	XVI	1		[49.294	172.25	28617	58054]
,, ,,	XVI	2		51.679	222.69	23207	44906
,, ,,	XVI	3		53.044	275.02	19287	36361
,, ,,	XVI	4		54 244	336.89	16101	29683

Isotherms of argon. TABLE 1*d*.

Date.	Series.	N°.	t	p	d_A	pv_A	v_A
March16,1910	XX	1	—120°.24	30.809	72.627	0.42421	0.013769
,, ,,	XX	2		33.776	82.816	40784	12075
,, ,,	XX	3		37.836	99.246	38124	10076
,, ,,	XX	4		41.668	118.51	35160	0.0084380
,, ,,	XX	5		44.510	136.31	32654	73363
March 5, ,,	XVII	1		47.705	165.79	28774	60317
,, ,,	XVII	2		50.351	206.57	24375	48410
,, ,,	XVII	3		52.253	280.25	18645	35682
,, ,,	XVII	4		53.191	338.95	15693	29503
May 4, 1910	XXVII	1	—121°.21	13.754	27.326	0.50333	0.036595
,, ,,	XXVII	2		17.225	35.283	48818	28342
March 17, ,,	XXI	1		30.122	71.459	42153	13994
,, ,,	XXI	2		34.070	85.580	39811	11685
,, ,,	XXI	3		37.465	100.33	37343	0.0099674
,, ,,	XXI	4		[41.932	123.85	33856	80741]
,, ,,	XXI	5		45.282	148.95	30402	67139
March 5, ,,	XVIII	1		47.094	170.05	27693	58805
,, ,,	XVIII	2		49.865	234.13	21298	42711
,, ,,	XVIII	3		50.885	333.75	15247	29963
Apr. 28, 1910	XXIV	1	—130°.38	12.773	27.394	0.46625	0.036504
,, ,,	XXIV	2		[14.384	31.583	45430	31663]
,, ,,	XXIV	3		15.664	34.726	45108	28797
Apr. 6, ,,	XXIII	1		22.861	55.807	40964	17919
,, ,,	XXIII	2		25.519	65.125	39185	15355
Jan. 7, ,,	XII	1		28.878	77.821	37108	12850
,, ,,	XII	2		[32.993	101.71	32438	0.0098318]
Apr. 30, 1910	XXV	1	—139°.62	11.986	28.122	0.42620	0.035559
,, ,,	XXV	2		14.586	35.573	41003	28111
Apr. 30, 1910	XXVI	1	—149°.60	11.150	29.183	0.38205	0.034266
,, ,,	XXVI	2		12.788	34.646	36910	28863

§ 6. A general survey of the region which the present isotherms in connection with earlier papers [1]) enable us to regard as known is given by the accompanying p, v_A-diagram for all observations [2]). Observed points are represented by small circles. For data for the boundary curve we may refer to the other papers just mentioned. Points calculated from the liquid and vapour densities are given by triangles [3]).

Finally, a diagram of the $\frac{pv_A}{T}$, d_A-isotherms is added to this paper [4]).

§ 7. *Individual virial coefficients*[5]).

An attempt was made to represent the isotherms by the empirical equation of state

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v^2_A} + \frac{D_A}{v^4_A} + \frac{E_A}{v^6_A} + \frac{F_A}{v^8_A},$$

and to evaluate the individual virial coefficients.

Seeing that we could not avail ourselves of measurements at such small densities as was the case with hydrogen and hence could not calculate values of A_A for each individual isotherm from the observations, the calculation was made by means of the equation

$$A_{A_T} = A_{A_0} \, (1 + 0.0036618 \, t).$$

A_{A_0} was first calculated as accurately as possible from

$$A_{A_0} = 1 - B_{A_0} - C_{A_0}$$

(since for $p = 1$, $v_{A_0} = 1$ and D_{A_0} etc. may be made $= 0$) and

$$pv_{A_0} = 1 - B_{A_0} - C_{A_0} + \frac{B_{A_0}}{v_{A_0}} + \frac{C_{A_0}}{v^2_{A_0}}.$$

---

[1]) Comm No. 115.

[2]) Fig. 5.

[3]) In order to make the diagram not useless long, the volumes above 0.040 are omitted. The isotherms of + 20°.39 C., 0°.00 C. and — 57°.72 C. therefore ought to have been drawn until the line $v_A = 0.040$.

[4]) Fig. 4.

[5]) Comm. No. 71 (1901).

And seeing on the other hand that the densities attained are not sufficiently great to allow of the calculation of the last coefficients, values of E_A and F_A and sometimes too of D_A (insofar as they had to be allowed for) were obtained by combining the critical magnitudes published a short time ago with the set of reduced virial coefficients VII. 1. Solutions for the other coefficients were then obtained for each isotherm from a number of suitable chosen points, and were tested with the observed results. Finally, correspondence was made as satisfactory as possible either by least squares or by the method of E. F. VAN DE SANDE BAKHUYZEN [1]).

In this way the individual coefficients for each isotherm given in table II were obtained. Numbers borrowed from the reduced coefficients VII. 1., are printed in italics.

Individual virialcoefficients of argon. TABLE II.

t	A_A	$10^3 B_A$	$10^6 C_A$	$10^{12} D_A$	$10^{18} E_A$	$10^{24} F_A$
+20°.39	+.107545	−0.60271	+0.66360	*+4.32836*		
0°.00	**+1.00074**	−0.73969	+0.00487	*+3.09635*		
−57°.72	+0.78922	−1.30460	+1.64016	*−0.67139*		
−87°.05	+0.68174	−1.63902	+2.12711	*−2.83014*	*+10.5566*	
−102°.51	+0.62511	−1.81649	+2.28125	*−4.10121*	*+10.4013*	
−109°.88	+0.59810	−1.92881	+2.57060	*−4.76310*	*+10.3251*	
−113°.80	+0.58372	−1.97263	+2.36239	+2.40001	*+10.2947*	
−115°.86	+0.57617	−2.03892	+2.74407	−2.15810	*+10.2837*	*−2.35600*
−116°.62	+0.57340	−2.02273	+2.56235	−1.20499	*+10.2806*	*−2.31432*
−119°.20	+0.56393	−2.04406	+2.31445	+0.65126	*+10.2759*	*−2.17669*
−120°.24	+0.56012	−2.05472	+2.50248	−0.67211	*+10.2764*	*−2.12239*
−121°.21	+0.55658	−2.05084	+2.37741	+0.13359	*+10.2783*	*−2.07246*

With these coefficients values of pv_A were calculated; table III gives percentage deviations of calculated from observed results. In this table [ ] and * have the same significance as before. Deviations placed between ( ) are so treated because the observations to which they belong were not used in the adjustment of coefficients; this was done from consideration of the difficulty of obtaining agreement with a formula of whose constants only three are derived from observations in that neighbourhood.

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[1]) Comm. No. 95*a* (1906).

Deviations of pv_A in percents of pv_A (C). TABEL III

d_A	O—C in %	d_A	O—C in %	d_A	O—C in %	d_A	O—C in %	d_A	O—C in %	d_A	O—C in %
+20°.39		0° 00		—57°.72		—87°.05		—102°.51		—109°.88	
20.499	—0.07	20.877	+0.03	23.509	+0.10	25.152	+0.21	25.571	+0.20	26.242	+0.21
25.759	+0.02	26.581	—0.03	[28.575	—0.17]	34.467	+0.06	35.077	0.00	34.807	+0.34
32.590	+0.16	32.302	+0.06	33.793	—0.06	55.822	—0,06	[47.893	+0.47]	65.142	+0.11
35.330	—0.07	37.782	—0.03	48.116	—0.03	71.444	—0.05	[53.752	+0.47]	*66.530	—0.24
35.759	—0.12	51.840	—0.04	64.948	+0.01	94.625	—0.16	62.240	+0.08	87.176	+0.01
47.319	—0.01	65.325	+0.02	90.695	+0.01	119.84	+0.12	[69.954	+0.48]	102.76	—0.25
59.134	+0.12							84,002	—0.13	125.56	—0.24
59.250	+0.01							95.802	—0.22	148.32	—0.17
								115.88	—0.22	*152.79	—0.46
								135.65	0.00	180.84	+0.31
								158.01	+0.31		
—113°.80		—115°.86		—116°.62		—119°.20		—120°.24		—121°.21	
67.078	+0.02	69.947	—0.20	26.480	+0.36	26.871	+0.32	72.627	+0.03	27.326	+0.20
88.889	+0.09	91.308	+0.27	34.939	+0.13	34.965	+0.34	82.816	+0.18	35.283	+0.21
06.68	—0.09	108.02	+0.07	68.630	+0.10	[70.314	+0.08	99.246	+0.12	71.459	—0.15
29.17	—0.03	131.51	—0.06	90.563	+0.03	70.481	—0.33	118.51	—0.02	85.580	—0.10
52.71	—0.03	155.12	—0.12	110.19	—0.22	*70,580	—0.23	136.31	+0.05	100.33	—0.36
55.40	+0.02	179.94	—0.19	133.69	—0.19	83.257	—0.23	165.79	—0.07	[123.85	—0.16]
32.13	+0.11	[183.35	+2.24]	159.71	—0.13	96.834	+0.24	206.57	+0.72	148.95	0.00
34.82	—0.03	235.47	+0.35	161.75	—0.23	98.863	—0.25	280.25	(+2.71)	170.05	0.00
12,99	+0.04	319.52	—0.09	[186.15	+0.14]	124.97	—0.20	338.95	0.00	234.13	(+1.95)
				210.02	(+0.52)	[143.71	+0.72]			333.75	0.00
				[260.61	+1.44]	156.36	+0.26				
				331.29	—0.05	[172.25	+1.68]				
						222.69	(+2.47)				
						275.02	(+4.12)				
						336.89	—0.12				

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BY

H KAMERLINGH ONNES,
Director of the Laboratory.

No. 119.

H. KAMERLINGH ONNES. "Further experiments with liquid helium. A. Isotherms of monatomic gases etc. VIII. Thermal properties of helium.

B. On the change in the resistance of pure metals at very low temperatures etc. III. The resistance of platinum at helium temperatures". (*With three plates*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **25 Februari 1911,** p. 1187—1208).

Eduard IJdo — Printer — Leiden.

H. KAMERLINGH ONNES. "Further experiments with liquid helium". **PLATE I.**

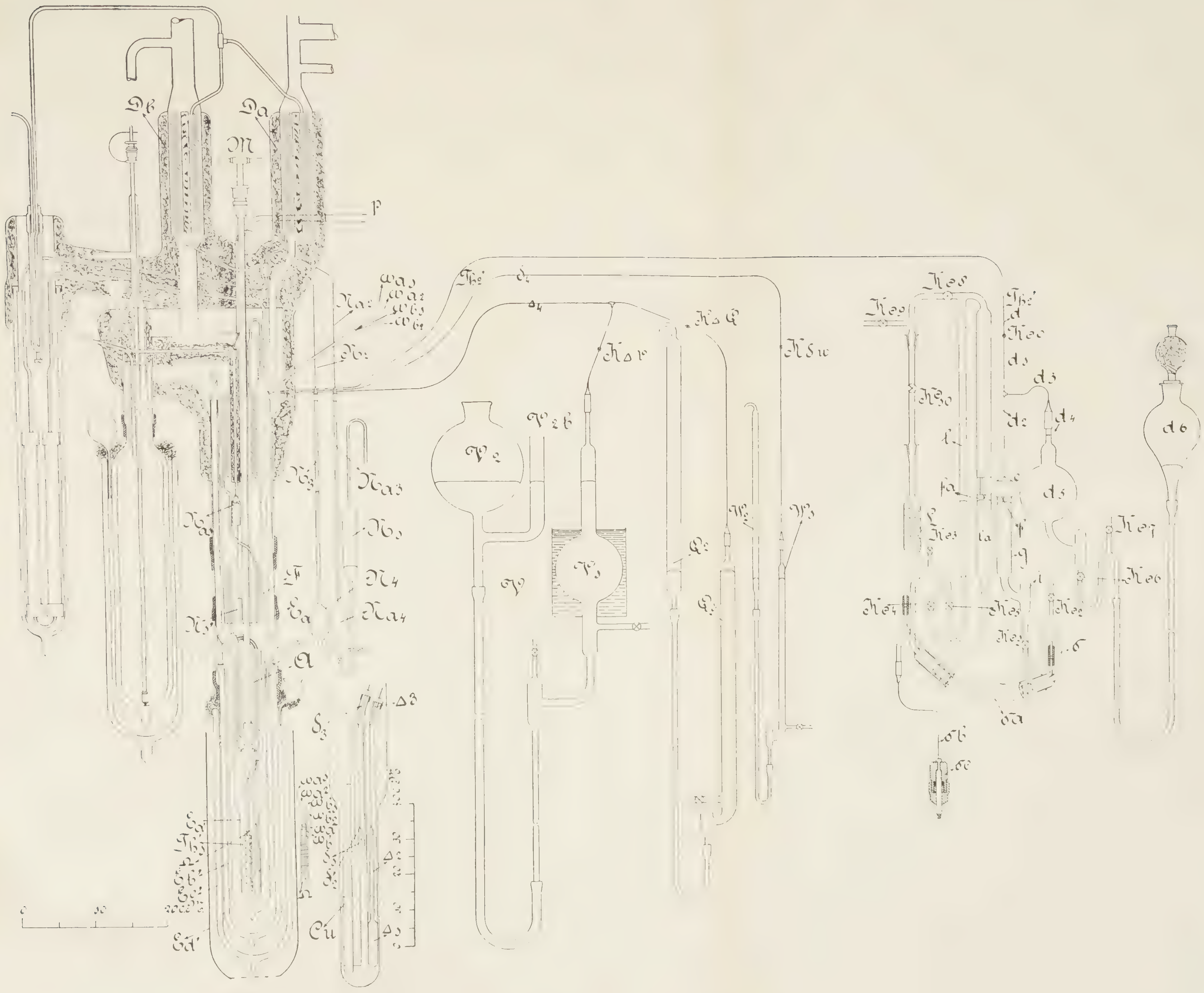

Fig. 1. Fig. 2.

Communication No. 119.

H. KAMERLINGH ONNES. "Further experiments with liquid helium".

PLATE II.

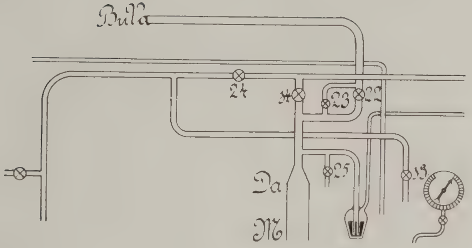

Fig. 1

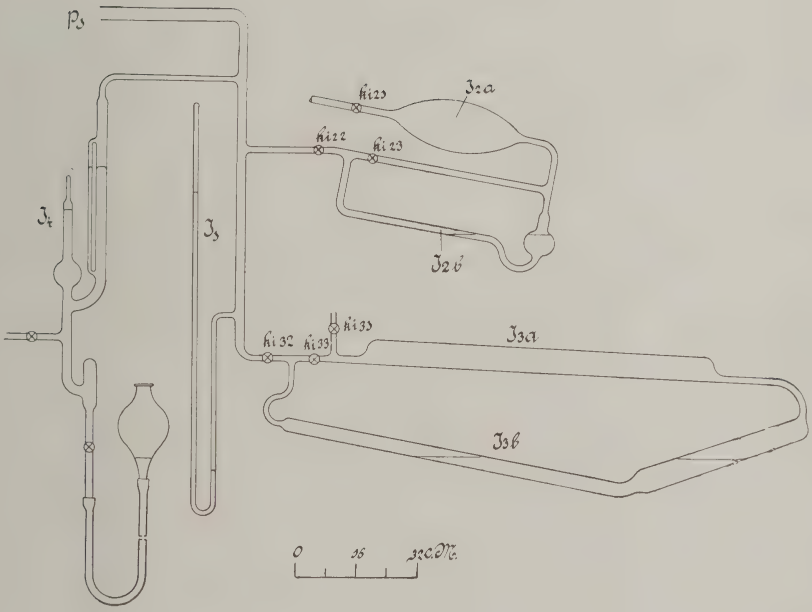

Fig. 2

Communication No. 119.

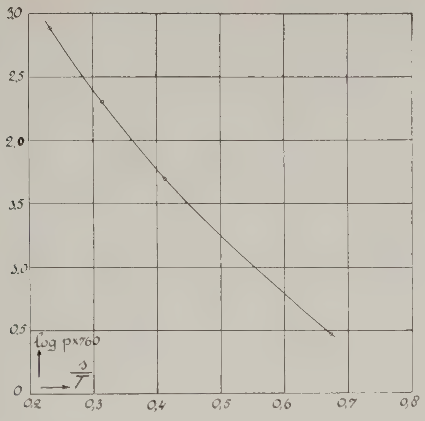

Fig. 1. Vapour pressure of helium.

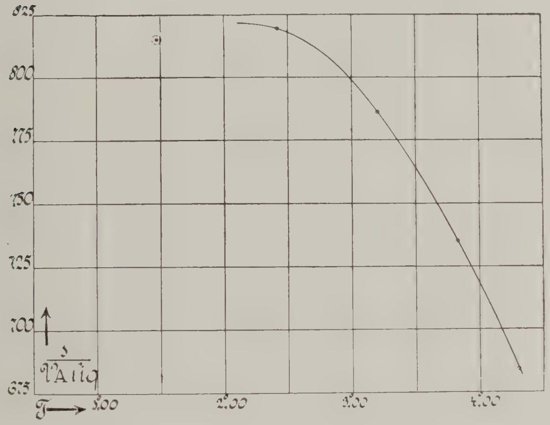

Fig. 2. Densities of liquid helium.

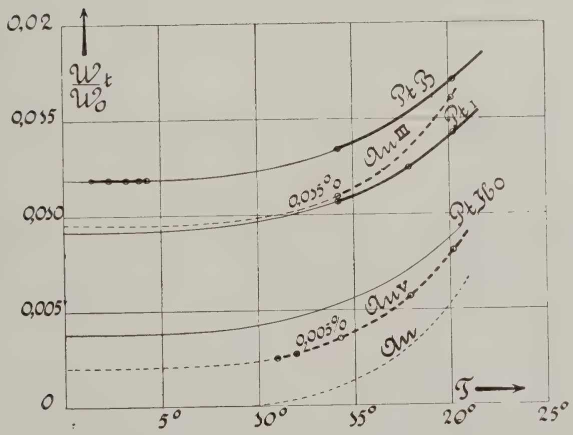

Fig. 3. Resistances of platinum.

Communication No. 119.

H. KAMERLINGH ONNES. "*Further experiments with liquid helium.*"

(Communicated to the Meeting of Dec. 24, 1910).

A. *Isotherms of monatomic gases etc.* VIII. *Thermal properties of helium.*

§ 1. *The Helium-bath.* In most of the experiments that one would like to make at helium temperatures, it is necessary to transfer the liquid helium from the apparatus in which it has been prepared to another — the helium cryostat — more suitable for holding the apparatus arranged for these special experiments. In Comm. N°. 112 (June 1909) it was mentioned that this was going to be tried; and in the Jubilee book presented to J. M. VAN BEMMELEN it was further stated that the transference had, in fact, been once successfully accomplished. Although the success which attended this operation allowed immersion in the protected helium bath of the apparatus with which it was shown that even at a vapour pressure as low as 0.15 mm. helium is still a liquid, it was nevertheless evident that this desirable result had been obtained only by accident. A method that promises to be more efficient is now being developed, and I hope to be able to make a communication in the near future concerning it.

In the meantime, a few problems could already be studied with the help of a liquefying apparatus resembling the original liquefying apparatus (Comm. N°. 108, Aug. 1908) sufficiently well to ensure that when an experimental apparatus is introduced into its interior this experimental apparatus would also be surrounded with liquid helium. To be certain that this was the case, it was necessary that the principle of the original liquefying apparatus should not be altered in any way, and, hence, the difficulty that the liquid helium would be contained in a space that is practically closed above by the regenerator spiral could not be avoided. But this space destined to contain the liquid helium could still be made as large as was found permissible from the experience gained with the liquefying apparatus. An apparatus was, therefore, constructed to hold a thermometer reservoir of greater dimensions than the one which had been used up till 1909, a resistance thermometer such as was used in the investigation of the electrical resistance at hydrogen temperatures, a dilatometer of dimensions greater than those given in Comm. N°. 112, and also a control dilatometer.

The apparatus is shown in Fig. 1 Pl. I [1]). The letters are the same as in Pl. III of Comm. N°. 108, and are accented where one of the parts has been modified. Moreover, Pl. II of that Communication holds for the helium cycle as far as its use at ordinary pressure is concerned. To allow the helium to evaporate under lower pressure the tube that leads the gas off from the liquefier is coupled to the wide exhaust of a BURCKHARDT vacuum pump capable of transplacing 360 m^3 per hour. To follow this operation the part D_a and those attached to it in Pl. II Comm. N°. 108 must be replaced by the modifications shown in Pl. II fig. 1; connection with the pump is made through *Bu Va* and this is closed by the tap 22; while 23 in a bypass allows a fine adjustment of the quantity of the gas that is being removed; 24 and 25 allow the gasometer and the liquefier to be independently evacuated (see Pl. II Comm. N°. 108).

Besides the changes in the apparatus necessary to enable it to contain the measuring apparatus, it remains to be remarked that a second helium thermometer Na_1, Na_2, Na_3, now serves to indicate the quantity of liquid hydrogen present in F instead of the two thermocouples that were formerly used in conjunction with the small helium thermometer (now N_1', N_2, N_3). The position of the liquid surface in F can be ascertained much more easily from the motion of the mercury in the capillaries N_3 and Na_3 than was possible with the more round-about thermocouple measurements; the liquid hydrogen can therefore be used more sparingly, and the tedious preparatory work of adjustment necessary for these experiments can be shortened.

In the lower part — the cryostat space — of the glass $E'a$ (fig. 1 and fig. 2) is the reservoir Th' of the helium thermometer, with which the temperature of the bath is determined, the resistance Ω, the dilatometer Δ, and the control apparatus of the dilatometer δ. And finally, a thick copper rod Cu is also placed in it so that, since the liquid in the bath cannot be stirred, conduction along the rod may keep the temperature of the bath more equable at all points. The narrow space between the regenerator spiral A and the wall of the vacuum glass Ea' is filled with flannel, and now three capillaries pass through it instead of the single thermometer capillary (that of Th_1 Pl. III Comm. N°. 108). One of these, Th'_2, leads to the thermometer (replacing Th_1, Th_2, Th_3, Th_4, of Pl. III, Comm. N°. 108), the second to the dilatometer (this was already used in Comm. N°. 112), and the third to the control apparatus of the dilatometer (connecting δ with W). Furthermore, instead of the two insulated wires of the thermocouple (Comm. N° 108) four insulated wires Wa_1, Wa_2, Wb_1, Wb_2, now pass through this space; these are the pairs of wires that lead the current to and from the resistance Ω.

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[1]) The alcohol glass with its attachments (cf. Pl. III, Comm. N°. 108) *Ed* is only partially shown in the drawing.

All these capillaries and insulated wires must pass through the space that is filled with liquid air, which must still remain airtight (this space is described under d of Comm. N°. 108 § 2, and b Pl. II of that Comm. shows how liquid air is introduced). This is accomplished by soldering the capillaries to the new-silver wall of the liquid air vessel, while the insulated leads are enclosed in new-silver tubes that pass through the wall and are soldered to it.

The operation of filling the lower portion Ea_1 (Pl. I fig. 1) with liquid helium is conducted in exactly the same way as is described in § 4 Comm. N°. 108. Practice in the various operations and the improvement made by introducing the second helium thermometer rendered it possible to save a fair amount of liquid hydrogen so that, as a part of the necessary hydrogen had been liquefied the previous day, it was possible to begin at half past seven in the morning and to have the cryostat part of the apparatus full of liquid helium by a quarter to two in the afternoon. The circulation pressure was kept at 25 atmospheres (cf. § 2, Comm. N°. 112).

The pressure under which the helium vaporizes is derived from the pressure obtaining in the wide space beneath the german silver chamber F; from this space a tube passes through F and comes outside the apparatus at p_1; it is there coupled to the apparatus for regulating and measuring the pressure. The difference of pressure between this space and the surface of the liquid helium necessary to drive the vapour up between the coils of the regenerator spiral was found, from measurements made with air, to be less than 1/20 mm., and may, therefore, be left out of account. Only at very low pressures will a correction be necessary for it in obtaining very accurate results.

Fig. 2, Pl. II shows the apparatus that serves to regulate the quantity of gas pumped off through the exit valves; by such regulation the temperature of the cryostat part of the apparatus is kept as constant as possible, and from its constancy one can judge how far the vapour pressure remains invariable; it also shows how this pressure is measured. For pressures greater than 5 cm. the gauge I_1 is used, for pressures between 5 cm. and 1 cm. I_2, and for pressures lower than 1 cm. I_3. By opening K_{i21}, K_{i22}, K_{i23}, or K_{i31}, K_{i32}, K_{i33}, I_{2a} or I_{3a}, as the case may be, is brought to a definite pressure which is measured by I_1 or by the MACLEOD gauge I_4; K_{i21} or K_{i31} is then closed, and the taps regulating the rate at which the gas is pumped off are operated so that the oil in the graduated sloping tubes of the indicators remains at the same mark.

Any definite pressure and, therefore, any definite temperature at the surface of the liquid in the cryostat can be quite satisfactorily obtained. The temperature of the bath, however, is less assured, since stirring is not possible, and the conductivity of *Cu* offers but slight compensation for this defect. The lower parts of the bath are at a higher temperature, and the corresponding vapour pressure may be increased by 0.009 to 0.011 mm. of mercury per mm. distance from the surface of the liquid helium; at the lowest temperatures this is equivalent to a temperature difference of 0.06 degree, and with this uncertainty we must be content as long as we have not at our disposal a cryostat in which stirring is possible; it is not, however, greater than uncertainties arising from other causes that are already present.

§ 2. *The Thermometer.* Temperatures were measured by means of a constant volume helium thermometer of zero pressure = 14.5 cm. (Cf. Comm. N°. 112).

At the lowest measured temperature, the pressure of the gas in the thermometer was 1.2 mm., and the vapour pressure of the helium was only 2 mm. The circumstances of measurement were, therefore, pretty much the same with respect to helium as if a constant volume ether vapour thermometer were used for determining ordinary atmospheric temperatures. In the present case there is, moreover, the particularly small value of the pressure itself to be taken into account. Hence, in the very nature of the determinations themselves there is cause for many uncertainties. In the meantime, however, it seems best to make a beginning by assuming that the ordinary gas laws may still be applied at the very small densities, and to postpone the application of corrections for the deviations that should differ from those according to the law of corresponding states and for possible condensation of vapour on the walls, etc., until experiments have been completed which will afford an estimate of these corrections. In this way one can at least attempt to obtain data concerning certain thermal properties of helium. I mentioned in Comm. N°. 112 that at that time I had not been successful in overcoming the difficulties that are always encountered when making measurements with a thermometer, built on the principle of the one that has hitherto been used, in the immediate neighbourhood of apparatus that are used for the preparation of liquid helium. These difficulties have not yet been wholly removed. The necessity for simplicity and ease of manipulation of the apparatus, and the fact that the thermometric measurements should be independent of all vibration and all disturbances arising from other operations are difficult to reconcile. But still, it would appear that the temperatures obtained may be relied upon to within 1/10th of a degree.

The part of the helium thermometer that serves for the adjustment of the constant volume, and for the reading of the pressure is shown on the right hand side of Plate I. Its arrangement is similar to that of the hydrogen thermometer shown on Plate I of Comm. N°. 95*e* (Sept. 1906) when this is being used for measuring hydrogen temperatures; part of the lettering is chosen so as to correspond with that of the latter plate. On account of the smallness of the pressures to be measured at the helium temperatures the space above the mercury in the adjustable double manometer tube l and f_a is evacuated, and, to make quite certain, they are connected to an evacuated tube L filled with charcoal and immersed in liquid air. The manometer tube on which the pressures are read off, has, as well as the adjusting tube, a small steel point, so that the difference of level between the two mercury menisci may be obtained with greater accuracy. The base e_a which carries the point f_a is slotted, as can be seen in the figure. Before making any adjustments the tap $K\theta_5$ is closed, and it is opened to allow communication between the mercury in the reading tube and that in the adjusting tube of the manometer only after the mercury meniscus in the adjusting tube has been brought to the level of the point f_a in the reading tube by opening $K\theta_1$ and moving the double manometer tube up and down until this is accomplished. Then to proceed to an adjustment the adjusting tube can be shut off with $K\theta_4$. By a slight turn of the screw s_c and of the screw with which the fine adjustment of the height of the manometer tube is obtained, both of which are within the observer's reach, the mercury surfaces are brought as near as possible to the two points; the height of the mid point between each point and its mirror image is then ascertained with the cathetometer provided with one of the reading microscopes of Comm. N°. 85 (June 1903) and of Comm. N°. 95*b* (June 1906) when the cathetometer was used as a vertical comparator.

In this way, taking account of the indications of the sensitive levels, heights may be measured accurately to within 0.002 mm. To eliminate the uncertainty in the correction for the refraction of light through the glass at the place where the point is under observation, and that in the correction for the temperature of the equilibrating mercury columns (as the capillary depression is only 0.01 mm. the uncertainty in it may be neglected) the tap $K\theta_0$ is introduced, and the spherical vessel d_5 forms part of the dead space [1]). If $K\theta_0$ is closed, and the mercury that stood in the narrow stem d_4 while the thermometer was being adjusted with $K\vartheta_6$ closed, is allowed to sink, there remains in the dead space only a very small and definitely known fraction of the total pressure, and the adjusting tube of the manometer must be lowered so as to bring the mercury levels once more to the two points. The displacement is read on a finely divided scale attached to the adjusting tube of the manometer, and at once gives in mm. of mercury the thermometer pressure for the temperature of the adjusting space, to which the only correction to be applied is that for the pressure remaining over.

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[1]) A coupling is inserted in the capillary d_2 by means of which many operations and controls are much more easily accomplished; it allows the whole manometer part of the arrangement to be loosened, and either that or the remaining apparatus may be connected independently with an air-pump, etc.

We need not stop to describe the different devices (cf. Comm. No. 60, June 1900) by means of which the various points to be seen are so arranged that they can be brought in succession in sharp focus into the field of the cathetometer; the significance of the air-traps in the mercury filled connecting tubes is sufficiently obvious from the figure, as is also that of the mercury filled rubber tube *Sa* surrounding the rubber connecting tube *S* and its junctions with the other tubes. On account of the comparatively large value of viscosity, equilibrium is, in general, reached but very slowly between spaces occupied by gas at such low pressures as those obtaining in our thermometer reservoir and in the dead space. In the present instance, however, the favourable circumstance arises that only a very small quantity of gas has to flow over, seeing that the dead space is extremely small. Against the widening of the capillary it may be urged that then the quantity of gas contained in it would lead to inaccuracy owing to the uncertainty existing regarding the distribution of temperature along it. After full consideration of the change of viscosity and density with temperature, and also of constructional difficulties, the low temperature portion of the capillary was made of 37 cm. steel capillary of 0.5 mm. bore, and the part that is at practically room temperature was made of 50 cm. copper capillary of 1.0 mm. bore. The resulting uncertainty is, then, at the most, 1 %, while the viscosity is not yet excessive, seeing that it is possible to adjust to 0.01 mm. within a period of 2 minutes.

§ 3. *Densimetric Apparatus.* The part of the dilatometer that was immersed in the helium bath consisted of a reservoir Δ_1

with a stem Δ_2, a narrow glass capillary Δ_3 continued by a steel capillary. The mass of helium here present was determined volumetrically in the bulb V_1 with a graduated stem both above and below, whose temperature was determined by that of the surrounding water bath; the pressure was read on a scale by using the branch V_{2b} of the mercury reservoir V_2. The dimensions of Δ_1 and V_1 are so chosen that the position of the mercury for the desired pressure can be read on the lower part of V_1's graduated stem before the dilatometer has been filled, and on the upper part after the filling has taken place. Moreover, the cross-section of the graduated stem has been chosen of such a size that when the dilatometer has been cooled again with $K_{\Delta v}$ and $K_{\Delta w}$ closed, after filling it at the boiling point to above the mark, the meniscus still remains in the stem even at the greatest densities employed.

Although the capillary is very narrow at the part where its temperature is uncertain, the correction for the gas condensed from it when the dilatometer is cooled (keeping $K_{\Delta v}$ and $K_{\Delta w}$ closed), which operates so as to cause a rise of the liquid meniscus in the stem, is of great importance when the question arises as to whether a maximum density can be shown to exist for helium or not. A second apparatus is therefore introduced having a very short stem and a similar capillary, but without a reservoir; to this the volumenometer W belongs. When the correction for the capillary of this control apparatus is calculated in exactly the same way as for the capillary of the dilatometer, it shows a rise of the level of the liquid that appears in the tube, and by comparing this with the observed rise one can obtain an indication of the accuracy of the correction.

For vapour density determinations the same dilatometer Δ_1 was used but along with the volumenometer Q; in this the gas was measured in a graduated tube, while it could be connected with Δ through $K_{\Delta Q}$ keeping $K_{\Delta v}$ closed.

§ 4. *Vapour Pressures of Helium.* The observed pressures have been corrected for the height of the helium surface above the middle of the thermometer reservoir $Th1'$. for the aerostatical pressure between the place where the pressure is measured and the surface of the liquid helium, and for the reduction of pressure due to friction along the coils of the regenerator spiral In this way the following values were obtained:

Helium, maximum pressure.			
Temperature.			$760\ p_{\text{coëx.}}$
I.	II.	mean.	
4°.29 K.	4°.28 K.	4°.29 K.	760
3.97			565
3.26	3.20	3.23	197
2.34	2.40	2.37	51
1.47	1.49	1.48	3

Columns I and II refer to two independent measurements.

In fig. 1 of Pl. III $\log p \times 760$ (where p is expressed in atmospheres) is graphed as a function of $\frac{1}{T}$. At the same time the figure gives us an idea of the agreement with the VAN DER WAALS vapour pressure law $\log \frac{p}{p_k} = f\left(1 - \frac{T_k}{T}\right)$ from which it would follow that the curve should be a straight line.

The curvature of the experimental curve is but small, but it is still clear that f decreases at the lower temperatures.

If f is calculated from the tangent at $T = 4°.29$ K. it is found that $f = 1.2$, $T_k = 5°.8$ K., while the two temperatures 4°.29 and 3°.23 give $f = 1.1$, $T_k = 5°.7$ K. At lower temperatures f becomes still smaller, and the mean value would be found to be only $f = 0.9$, from which it would follow that $T_k = 6°.4$, a value that, considering the temperature of the BOYLE point, must certainly be too high.

It is worth remarking that this value of f differs very much from the values, ranging from 2 to 3, that have been found for ordinary normal substances 1). Helium, then, shows in a greatly exaggerated form the deviation from the mean $f = 2.7$ for ordinary normal substances that is already noticeable in the case of substances whose critical temperature lies below 0° C. which give a value $f = 2.2$. Associative substances deviate in the opposite direction; for instance, for water $f = 3.26$ and for isobutyl alcohol $f = 4.17$.

The new light now thrown upon the vapour pressure law for helium also allows a new estimate of the lowest temperatures that were reached in the experiments published in the van Bemmelen Jubilee book, which were then estimated upon a basis of $f = 2.2$. With the value now obtained, the temperature for a vapour pressure of 1 mm. should be 1°.33 K., and for 0.15 mm., which was the lowest pressure reached, the temperature should be 1°.15 K., while, to reach a temperature of 1° K., the vapour pressure would have to be lowered to 1/25 mm.

§ 5. *Densities of Liquid Helium.* In the following table containing the experimental results, densities are expressed in terms of the normal density of the gas.

Helium, liquid densities.				
T	$\frac{1}{v_{A\mathrm{liq}}}$			
	I.	II.	III.	readjusted.
4° 33 K.	[658 0]			678.0
4°.29		682.3		682.3
4° 28			683.6	683.6
3°.98		715.5		715.5
3° 26		779.0		782.0
3.°20	784.8		785.9	785.9
2°.40	822 6		818.8	818.8
2° 34		815.4		820.0
1° 49			815.3	815.3
1° 47		810.9		815.0

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1) Kuenen, Zustandsgleichung p. 142.

From these values ρ_{liq} is obtained by multiplying by $\rho_{0^\circ\ \text{C. 760 mm.}} = 0.0001787$, so that we now get $\rho_{\text{liq coëx } 4^\circ.29} = 0.122$, where the roughly approximate value 0.15 was given before.

The great decrease in the expansibility as the temperature is lowered is remarkable. In the experiments of 1909 described in Comm. N^0. 112 the impression had already been created that this would prove to be the case; the density values then obtained are given in column I. The results are shown graphically in fig. 2, Pl. III, and it is particularly noteworthy that there seems to be a maximum in the density; from the figure this seems to be at about 2°.2 K. Furthermore, it was clearly observed that, when the temperature was being lowered and passed 2°.1 K., the meniscus in the stem of the dilatometer became stationary, and rose again as the temperature sank further to 1°.48 K., while the reverse phenomenon was observed as the temperature rose again from this point to 2°.37 K. The following results show that the meniscus really stands lower in the stem at 2°.37 K. than at 1°.48 K. and that this is not due to the influence of condensation of gas from the dilatometer stem.

First experiment.

Temperature.		Position of the meniscus.	mean	
1°.47 K.			0.72	
2°.34	before cooling	0.52		
	after cooling	0.49	0.505	
		difference	0.215	
		correction	0.06	difference 0.155

Second experiment.

Temperature.		Position of the meniscus.	mean	
1°.49		0.59		
		0.58	0.587	
		0.59		
2°.40		0.42		
		0.37	0.393	
		0.39		
	observed minimum	0.35		
		difference	0.194	
		correction	0.082	difference 0.112

An idea of the accuracy of the corrections applied in each case may be got from the fact that, in the second experiment, the control dilatometer showed a rise of the meniscus of 0.03 as the temperature fell, while the calculated value was 0.028 The mean number 0.134 that remains after the correction has been applied, must be ascribed to expansion between 2°.37 K. and 1°.48 K. As far as a conclusion could be drawn from the observation, a maximum density point for helium has to be accepted. From a single observation in which the vapour pressure of the bath was lowered to 1 mm. it would have followed that no further expansion occurs as the temperature is lowered still more; but, in the meantime, this one observation, during which the bath was not stirred, is too uncertain to allow a definite conclusion as to whether or not the density of helium after attaining a maximum decreases till it reaches an invariable value.

§ 5. *Vapour Densities of Helium.* The density at a pressure of 65.54 cm. and a temperature of 4°.29 K. was found to be 69.0 times the normal density. Calculating B from the equation $pv - RT = B/v$, we get $B = -0.000047$; and, for the density of the saturated vapour at a pressure of 76 cm. a value of 85.5 times the normal. The correction for C to be applied according to the mean reduced equation of state VII. 1, although undoubtedly appreciable, appears to be too uncertain At 3°.23 K. by extrapolating values of the individual B's deduced from the helium isotherms between 0° and — 216°.56 C. (Comm. N⁰. 102*a*, Dec. 1907) B was found to be -0.000061, and this gives at 3°.23 K. a saturated vapour density 24.5 times the normal.

From these values various characteristic thermal data may be calculated for helium. If we deduce the slope of the Mathias diameter from 4°.29 K. and 3°.23 K. we find $-b_d = 0.0033$, and, taking the critical temperature to be 5°.5 K. and hence reaching the value $\rho_{kd} = 0.065$ we get for the constant of the Mathias diameter $-\mathfrak{b}_d = 0.255$. Mathias foretold that the value of $-\mathfrak{b}_d$ would be small, and he suspected that it would be 0.14. The first part of his remarkable prophecy is, therefore, hereby fulfilled.

For the critical virial ratio $K_4 = \frac{RT_k}{p_k v_k}$ we get (taking $T_k = 5°.5$ K., and $p_k = 2.75$) from ρ_{kd} a value 2.68, which is almost exactly the theoretical value deduced from the van der Waals equation of state. The value of this constant is thus markedly smaller for helium than for all other substances, with the exception of hydrogen, in which case it can be obtained only from very uncertain calculation yielding the result 2.9. (See Kuenen l. c. p. 60). The smallest known value is the one recently obtained for oxygen by E. Mathias and H. Kamerlingh Onnes viz. 3.43. (Comm. N°. 117, June 1910). In a paper that will soon be published by C. A. Crommelin and H. Kamerlingh Onnes[1]) a deduction from the isotherms of $K_4 = 3.28$ for argon will be given.

§ 6. *Molecular Attraction in Helium.* The occurrence of a maximum density in a substance of such simple constitution as helium gives rise to questions of great import from the point of view of molecular theory. With a substance like water it is easy to imagine a particular molecular combination by which some of the parts are more closely united, while others are separated, the whole leading to an increase of volume as the temperature is lowered, and this especially when one considers that the dielectric properties of water probably play a part in the phenomenon. But helium atoms we are forced to consider as spherical and smooth, and, as appears from the Zeeman effect for helium, of the simplest possible internal construction; and for their case we seek in the meantime in vain for a basis for a similar explanation. Moreover, helium differs from ordinary normal substances, but in exactly the opposite way to that in which associated substances differ from them.

A dissociation increasing as the temperature is diminished, leading to an increase of the number of molecules (and, therefore of R in the equation of state), which would account for this deviation in the opposite sense, can scarcely be imagined. Should it appear that the change was occasioned by an increase in the dimensions of the helium atoms (that is, of b in the equation of state) as the temperature is lowered, then this, too, would be something strikingly unusual. The behaviour of helium seems rather to make it clear that even in the case of ordinary normal substances two different kinds of molecular attraction must be distinguished from each other — an attraction of comparatively large sphere of action, and an attraction that is local, but more intense, of smaller range, and confined to the immediate neighbourhood of the surface of the molecule; this latter attraction causes ordinary normal substances when compared with helium to resemble rather associative substances; in the case of liquid helium the latter type of action of the attraction would, then, be suppressed.

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[1]) Comm. N°. 120*a*, Proceedings of this Meeting.

If it is not, indeed, entirely absent in helium, the sphere of influence of this force must have wholly withdrawn within the space occupied by the atom at the lowest temperatures (which is probably also to a large extent the case for substances like hydrogen at the lowest temperatures at least); and, therefore, the predominance of characteristics which are just the reverse of those in associative substances leads to the supposition that in our case a part of the attraction diminishes with the temperature. Even this idea is at first sight strange, for we are familiar with the idea of attraction increasing as temperature falls. According to BOLTZMANN's law this increase must take place in a perfectly definite manner, even for a constant attraction between the molecules. When, therefore, we assume a decrease in the cohesion this must exist notwithstanding the cause for increase given by BOLTZMANN's law. It would, perhaps, be due to the fact, that at lower temperatures the decrease in the attractive force originating in the helium atom would predominate.

Let us work out a little further a modification that will affect the behaviour of the substance in such a way as to decrease the attraction, the a of VAN DER WAALS, with the temperature decreasing below a certain temperature. Its importance is far more radical than that which occasions an increase, for, while the latter changes the phenomenon more in degree, the former can occasion a fundamental alteration.

A few simple illustrations may illustrate this point. For the sake of simplicity let us take the VAN DER WAALS equation of state. Putting a and b constant for higher temperatures so that T_k can be calculated, and putting also the attraction $a = KT$ from $T = 0$ to $T = T_k$ and, therefore $a = KT_k$ at T_k, it follows then, in such a simple manner that it is not necessary to write down the equations here, that all temperatures below the critical T_k show the critical phenomena for $v = 3b$, the critical pressure being for every temperature proportional to the absolute temperature, viz. $\frac{1}{27}\frac{KT}{b^2}$. With respect to the individual isotherms, the gas above T_k behaves as a VAN DER WAALS substance, in correspondence with our assumption $a = const.$, but, for every temperature T below T_k, the isotherms are determined by taking the isotherm of T_k and shortening its ordinate in the ratio of T to T_k.

Assuming now that $a = KT$ holds only up to a certain temperature $T_1 < T_k$, and that $a = const.$ is the law from $T > T_1$ onwards, then the isotherms from the critical temperature to T_1 are determined from the equation of VAN DER WAALS, and from this equation, too, are determined the maximum vapour pressure, and liquid and vapour densities. Isotherms for lower temperatures are then determined from these by taking the ordinates for each volume from the isotherm for T_1 and diminishing it in ratio of T to T_1. The densities of coexisting liquid and vapour phases would thus remain unaltered, while their common pressure would be simply proportional to T. Although with helium the maximum vapour pressure diminishes less rapidly with the temperature than is the case with ordinary normal substances, the diminution is still very much greater in reality than would be the case under the conditions above assumed.

A substance that fulfilled these conditions would, moreover, exhibit some other very unusual properties. The energy change at constant temperature would be zero, the latent heat of vaporization would alone be necessary for external work, and so the internal latent heat of vaporization would be zero.

To realise the significance of the modifications which the thermodynamical properties of a substance undergo when the molecular attraction decreases with the temperature, let us assume that it decreases more rapidly than in simple ratio; in that case one is brought to the deduction of still stranger properties. We may here mention the case in which $a = cT^2$ for temperatures below $T_1 < T_k$. With such a substance at a temperature beneath T_1, lowering of the temperature would diminish the difference between the liquid and vapour densities, and this difference would disappear at a temperature T_{ki} determined from the conditions $\frac{dp}{dv} = 0$ and $\frac{d^2p}{dv^2} = 0$ by the equation $T_{ki}\ T_k = T_1^2$. Hence, an *inferior critical point* occurs from which to the absolute zero the substance once more behaves as a perfect gas. For this case the change of energy with volume is negative, and so too is, therefore, the internal latent heat.

We have still to examine if there are further assumptions which are consistent with a decrease in the molecular attraction as the absolute zero is approached.

The nearest comes in this respect KELVIN's and J. J. THOMSON's idea of the structure of atoms. Assume, for example, that an atom consists of a sphere of uniformly distributed positive electricity inside which is an electron; then two such atoms would, at the absolute zero where the electron comes to rest, exert no electrical attraction upon each other. As soon, however, as the electrons begin to oscillate about their positions of equilibrium, and begin to describe orbits about their centres, attraction begins to be felt. An investigation similar to those made by VAN DER WAALS JR. based upon the principles of statistical mechanics would be necessary before one could say how the molecular attraction of a system of such atoms would depend upon the effects of collisions and of temperature radiation (they are, in fact, vibrators such as those assumed by PLANCK and EINSTEIN). *A priori*, it seems to be not impossible that a increases over a definite temperature region as the temperature rises.

In the meantime all these theories do no more than emphasise the fact that the behaviour of helium forces us to question the significance of the absolute zero with respect to molecular attraction. Hence it is of first consequence to obtain data concerning the thermal properties here mentioned in connection with helium that would lead to the solution of these problems, and also to investigate related properties such as capillarity, viscosity, specific heat, refractive index and dielectric constant, for which data are still lacking. For this purpose the solution of the problem of transferring liquid helium to a vessel in which the regenerator spiral no longer interferes with the introduction of measuring apparatus is absolutely essential.

B. *On the change in the resistance of pure metals at very low temperatures, etc.* III. *The resistance of platinum at helium temperatures.*

§ 1. *The resistance of a wire of very pure platinum at helium temperatures.* As soon as the possibility had been attained, it lay at hand to extend to helium temperatures the investigation of the change of electrical resistance of pure metals that, in Comm. No. 99*c* (June 1907), had been brought down to the lowest hydrogen temperatures. For this purpose the resistance Pt_B which had been calibrated at hydrogen temperatures as well as at others with the resistance Pt_I of Comm. No. 99*b* (June 1907) was available It was constructed on the model of Pt_d (Comm. No. 99*b* § 2), and is indicated by Ω on Plate I of part *A* of the present paper, fig. 1. The thin platinum wire is wound round a glass cylinder and is kept tight on it by being wound while hot, and the thicker platinum ends W_a and W_b are fused to the glass. To these ends the double platinum leads W_{a_1}, W_{a_2} and W_{b_1}, W_{b_2} are attached; they are not, however, welded in the blowpipe, but are simply tin-soldered. The resistance was measured on the WEATSTONE bridge according to the method described in Comm. No. 99 and previous Communications The ratios of w_t, the resistance at the temperature of the observation, to w_0, that at 0° C., are here given.

Resistance of platinum wire Pt_B

T	$\frac{w_t}{w_0}$
273° 09 K.	1
20.2	0.0171
14.2	0.0135
4.3	0.0119
2.3	0.0119
1.5	0.0119

From this it appears that by descending to helium temperatures the resistance is still further diminished, but when these temperatures are reached the resistance attains a constant value quite independent of the individual temperature to which it has been brought. The results are plotted in fig. 3 Pl. III, which shows well the asymptotical approach of the resistance to a constant value at 4°.3 K.

§ 2. *The probable resistance of pure platinum and of pure gold at helium temperatures.* In order to establish the exact significance of the result just obtained we must take account of the fact that the wire Pt_B was not made from quite pure metal, and we must allow for the probable influence of this difference from pure platinum.

With this end in view, we shall first confine our attention to the observations that have been made upon gold (Comm. N⁰. 99). Remembering the close resemblance between the differences of the resistances of platinum and of gold wires from a linear function of the temperature, we may, in view of the result that has been obtained with platinum, extrapolate the Au_V resistance curve to give a constant value at helium temperatures. This has been done in fig. 3 of Plate III. The parts of the curves obtained from observations are drawn with thicker lines. We now note that, according to § 1 of Comm. N°. 99*c* by KAMERLINGH ONNES and CLAY (June 1907) the influence of admixtures can be represented with rough approximation even down to hydrogen temperatures by an additive resistance that is independent of the temperature. In this way the line correspondingly marked in the figure was obtained for Au_{III} which was constructed of gold of a smaller degree of purity (0.015 % admixture against 0.005 % for Au_V). According, now, to § 1 of Comm. N°. 99*c* the effect of admixture should be pretty well proportional to the quantity present, and this would lead to negative values for pure gold. In the first place, however, we do not know if the impurity was the same in the two cases, nor do we know the influence of possible tensions in the metal; but moreover, such great uncertainty exists in our rough approximations as to confine our most probable result in the meantime to this: That within the limits of experimental error (the degree of purity attainable) the resistance of pure gold is already zero at helium temperatures.

Let us return to platinum. The wire Pt_B seems to be less pure than Pt_I (see table V of Comm. N⁰. 99*b*), and, moreover, the fixing of the wire on the glass may give rise to undesirable effects. By putting the additive resistance once more constant, to a first approximation, extrapolation gives for Pt_I the corresponding line shown in the graph. But still, the resistance of Pt_I may not without further comment be regarded as the resistance of pure platinum. A wire of greater diameter used by HOLBORN gave a greater relative decrease of the resistance from 0° to — 191° C. If we extrapolate these values to lower temperatures the resistance remaining at helium temperatures, and independent of any further change of temperature, would be nearer zero. One may ask if it is not possible to put the difference between the two wires obtained from HERAEUS inversely proportional to the thickness and in that way deduce a value for pure platinum unaffected by the individual treatment of each; but this method would lead us too far into the region of pure conjecture. But still, the conclusion seems to be fully established that the resistance of pure platinum is, within the limits of experimental error — the attainable degree of purity — already zero at helium temperatures.

§ 3. *The change with temperature of the resistance of pure metals at low temperatures.* I was formerly of the opinion that the resistance of pure metals reaches a minimum as the temperature is diminished, and then, as the temperature sinks still further, again begins to increase and becomes infinitely great at the absolute zero; but now it seems to me to be more probable that, even before the absolute zero is actually reached, the resistance if not zero, has become so extremely small that it practically vanishes, and that this remains the case for further lowering of the temperature.

In view of this result, then, we must also abandon the theory that has served for years as a guide in our Leiden researches upon the resistance of metals at low temperatures, according to which it was imagined that the resistance would attain a minimum as the temperature was lowered and would become infinitely great at $T = 0$, in consequence of the assumption that the electrons which are the actual conductors in metals would, as was expressed by me in 1904, begin to precipitate on the atoms as a vapour on being cooled to hydrogen temperatures, or as KOENIGSBERGER — in a manner leading to a similar dependence upon temperature — explains the phenomenon that was then supposed to exist, by the recombination of the electrons that had been freed by dissociation. I already questioned the validity of this assumption with respect to its application to perfectly pure metals at hydrogen temperatures, when the latest experimental results (Comm. by KAMERLINGH ONNES and CLAY) obtained with extremely pure gold showed that the point of proportionality would always have to be sought at still lower temperatures. It is now quite clear that in the case of metals like gold and platinum at any rate that theory must be dropped. It seems that the free electrons in the main remain free, and it seems to be the movable parts of the vibrators that are now bound, their motion at ordinary temperature forming the obstacles to conduction; these disappear when the temperature is lowered sufficiently as the vibrators become practically immovable [1]). There is, in the meantime, no occasion to calculate, unless for still much lower temperatures which cannot just yet be realised, a "latent heat of vaporization" or a "dissociation constant" for the electrons for the case of pure metals of the type treated.

The marked decrease in the resistance until it becomes practically zero at a temperature just above 4°K. and its remaining at this value as the temperature is lowered further as has been shown over a range of about two and a half degrees, so that, as far as resistance of these metals is concerned, the boiling point of helium is practically the absolute zero, points in another direction. It seems to me to be connected with the change with temperature of the heat energy of molecular motion of solid substances that has been deduced by EINSTEIN in his theory of the specific heats, on the assumption that it is the energy of vibrators determined by radiation equilibrium.

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[1]) That the vibrators become practically immovable represents what we have formerly called the "freezing" of the electrons.

In particular an obvious assumption to make is that the mean free path of the electrons which provide conduction is determined by the elongation of the above mentioned vibrators. To further illustrate this point let us keep as closely as possible to the theory of electrical resistance of RIECKE ¹), DRUDE and LORENTZ, who has developed it into a pure theory of electrons. We take the formula

$$\gamma = \frac{1}{3} \frac{\varepsilon^2}{c^2} \frac{NL\mathfrak{g}}{\alpha T}$$

where γ is the electrical conductivity of a cube of unit volume, N the density of the free electrons, L their mean free path, $\mathfrak{g}$ their molecular speed, and c the speed of light, ε the elementary charge and $\alpha\ T$ the kinetic energy of a free electron while T is the absolute temperature. Putting $p = \frac{1}{3} \frac{\varepsilon^2}{C^2} \frac{\mathfrak{g}}{\varkappa \sqrt{T}}$, this becomes

$$\gamma = \frac{pNL}{\sqrt{T}}$$

and according to RIECKE if $q = \frac{\mathfrak{a} \sqrt{T_s}}{\pi (1 + \beta s)^2}$, where $\mathfrak{a}$ is the distance between the atoms supposed te be cubically arranged, s the ordinary and T_s the absolute temperature of the melting point, β in RIECKE's notation the coefficient of linear expansion, $L = \frac{q}{\sqrt{T}}$. Instead of this hypothesis of RIECKE's we shall put $L = \frac{q'}{\sqrt{E_T}}$

in which
$$E_T = 3R \frac{\beta\nu}{e^{\frac{\beta\nu}{T}} - 1}$$

where $\beta = 4.864 \times 10^{-11}$, now represents, according to PLANCK, the energy of a vibrator whose frequency is ν. The product $\beta\nu$ we will call as usually is done a.

We then get for the ratio of the conductivity γ_T at any temperature T, to γ_0 that at 0° C. the value

$$\frac{\gamma_T}{\gamma_0} = \frac{\sqrt{T_{0^\circ C.} E_{0^\circ C}}}{\sqrt{T E_T}}.$$

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¹) RIECKE, Physik. ZS. 1909, p. 512.

This formula gives, in fact, good expression to the decrease with temperature of the resistance of pure metals of the kind here considered (monatomic ?). It shows in the first place the decrease to zero at a temperature above the absolute zero. For $\beta\nu = a = 54$ the resistance at helium temperatures becomes about 0.0001 times that at 0° C.

If we may further assume that $\frac{a}{T}$ is already small at 0°C., then the resistance w_T at T in terms of the resistance w_0 at 0°C. becomes

$$\frac{w_T}{w_0} = \frac{T - \frac{1}{4}\,a}{273.1 - \frac{1}{4}\,a}.$$

In fact, at 0°C. the temperature coefficients of the resistances of pure metals are, as a rule, greater than 0.00367, and, for platinum, gold, silver and lead they lie in the neighbourhood of 0.0039 and 0.0040.

And lastly, the formula also expresses well the fact that the diminution of resistance diminishes in quantity at hydrogen temperatures, and that in greater degree for substances of high melting point than for those of low melting point.

An accurate numerical equation, however, such as to determine even the bend in the curve that represents the resistance as a function of the temperature can be obtained only on the assumption that smaller values of ν and, therefore, of a come in the front at lower temperatures. Definite values, indeed, cannot be ascribed to ν. EINSTEIN [1]), for instance, deduces from its elasticity $a = 200$ for silver (for he gives $\lambda = 73.10^{-4}$ cm. for the wave-length in vacuum corresponding to ν), while NERNST [2]) from the specific heat, deduces the value $a = 162$ corresponding to $\lambda = 90.10^{-4}$, a number, however, which is not of itself sufficient to represent the wole behaviour of silver. For lead, **Nernst** gives $a = 58$, while **Einstein** gets $a = 108$ from the elasticity. Moreover, according to the elasticity a should increase somewhat at lower temperatures, while, from the specific heat, it would appear that the change should take place in the same sense as that in which the resistance changes. This, too, shows that the theory is still far from perfect.

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[1]) A. EINSTEIN. Ann. d. Phys. (4) 34 (1911) p. 170. Since the address delivered in the December meeting was only ready for printing in the number of the Dutch Proceedings for Febr. 1911 I have been able to add then the following calculations from the elasticity to what I communicated in December.

[2]) Cf. also MADELUNG, Gött. Nach. 1909, p. 100, who was the first to calculate the period of molecular vibrations.

As there exists so much uncertainty, and as it is more a question of showing that the introduction of vibrators leads to a qualitative explanation of the sense in which the observed change of resistance deviates from proportionality to temperature, I have taken for a one half of each of the values obtained by **Einstein** from the elasticity. In this way we obtain for a:

for Pt 111, Ag 100, Au 92, Pb 54.

		$\frac{w_T}{w_0}$							
T	$\frac{T}{273.1}$	platinum		silver		gold		lead	
		C	O	C	O	C	O	C	O
372°.86	1.365	1.405		1.401	1.411	1.397		1.384	
273.1	1	1	1	1	1	1	1	1	1
169.29	0.617	0.579	0.581	0.583	0.581	0.586	0.593	0.601	0 594
77.93	0.285	0.213	0.199	0.220	0.197	0.225	0.219	0 250	0 253
20.18	0.074	0.012	0.014	0.015	0.009	0.018	0.008	0.035	0.030
13.88	0.054	0.003	0.010	0.004	0.007	0.005	0.003	0.015	0.012
4.30	0.016	0.000	[0.009]	0.000		0.000	[0.002]	0.000	

It appears, therefore, that there is indeed a qualitative correspondence [1]. Before we can attach any greater importance to it, however, it would have to be shown that the ratio of heat conductivity to electrical conductivity at hydrogen temperatures [1]) satisfies the conditions imposed by RIECKE's modified theory [2]).

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[1] The numbers are all taken from the Leiden observations (**Kamerlingh Onnes** and **Clay** l. c.) and they refer to the purest of the wires, while the probable negative correction for the influence of admixture and for the results of treatment during manufacture necessary for its expression in terms of the pure metal have been omitted. The influence of admixture is such as to give rise to impediments distributed, at distances determined by the quantity of admixture present, throughout the metal, which exert an influence

At all events in developing new theoretical considerations it seems desirable to take into account the result obtained [3]).

I gratefully record my indebtedness to Dr. C. DORSMAN for his intelligent assistance during the whole of this investigation, and to Mr. G. HOLST, who conducted the measurements with the WHEATSTONE-bridge with much care

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upon the mean free path of the free electrons, that is proportional to $\sqrt{T}$ and therefore an influence on the resistance that is independent of the temperature, just as mixed crystals do in alloys.

Estimating for mercury $a = 30$ on account of its lower melting-point, we get the following multiples of the value extrapolated to 0° C. from observations on the solid state (loc. cit.).

T =	77°.93 K.	20°.18 K.	13°.88 K.
calculated	0.263	0.050	0.027
observed	0.279	0.056	0.033

[1]) Experiments to elucidate this point have been in preparation for some time.

[2]) An assumption that may obviously be made is that the energy of the vibrators determines the increase of volume from the absolute zero, with which the explanation of the relation between expansion and change of resistance on one hand, and between expansion coefficient and specific heat on the other hand, deserves to find a place in the theory.

[3]) The further question calls for attention that is suggested by it regarding the peculiarities of the motion of electrons through conductors when, by taking all precautions, the mean free paths are as large as must, in the meantime, be assumed that they can be made (and begin to be comparable with the thickness of very thin layers).

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

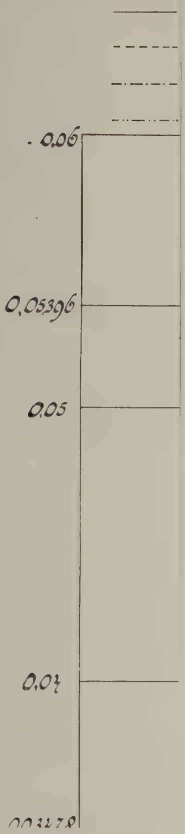
No. 120a.

H. KAMERLINGH ONNES and C. A. CROMMELIN. „Isotherms of monatomic substances and of their binary mixtures. IX. The behaviour of argon with regard to the law of corresponding states". (*With a plate*).

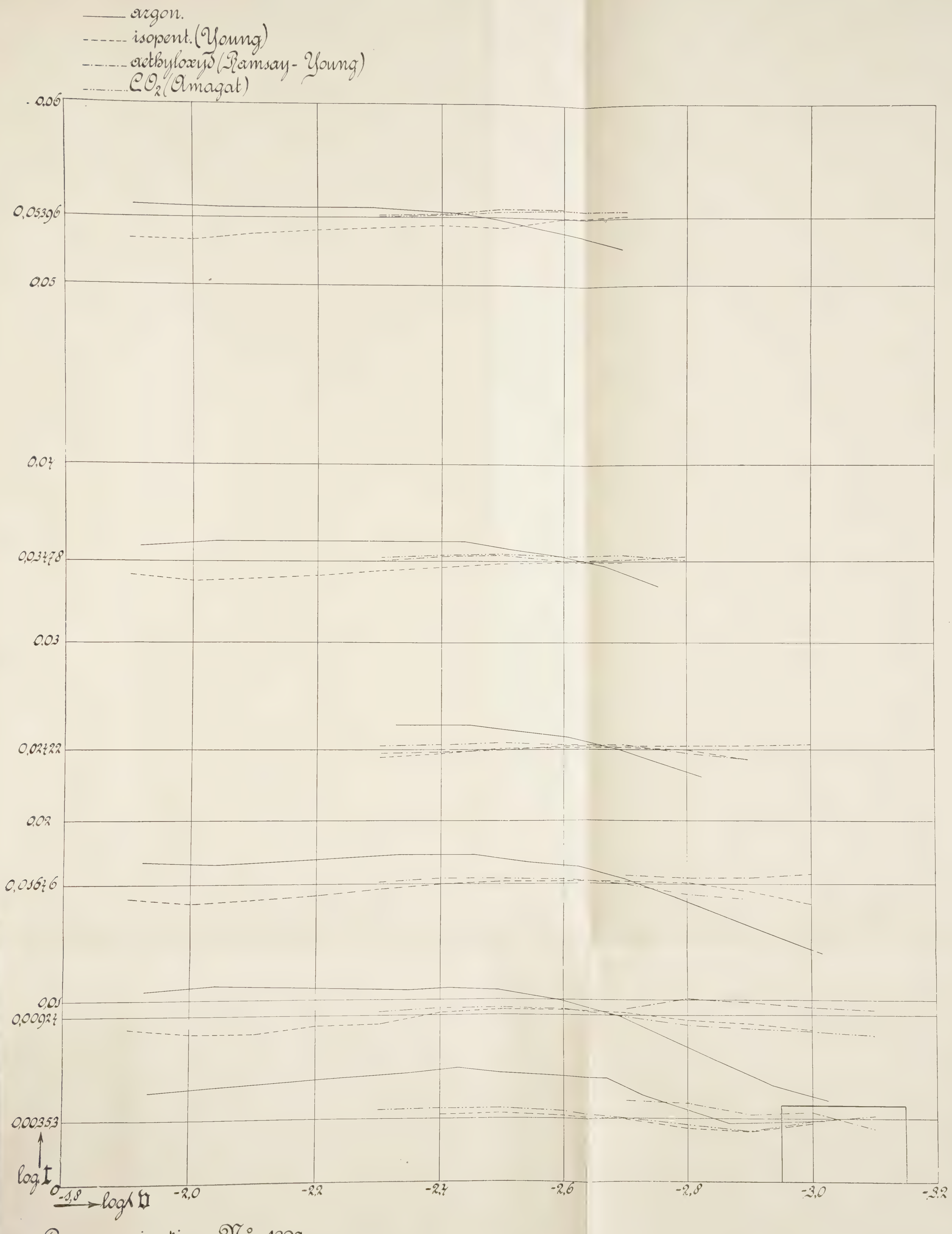
(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, **25 Februari 1911**, p. 1177—1187).

Eduard IJdo — Printer — Leiden.

H. KAMER



H. KAMERLINGH ONNES and C. A. CROMMELIN. „Isotherms of monatomic substances and of their binary mixtures. IX. The behaviour of argon with regard to the law of corresponding states."



Communication No. 120a.

H. KAMERLINGH ONNES and C. A CROMMELIN. — "*Isotherms of monatomic substances and of their binary mixtures.* IX. *The behaviour of argon with regard to the law of corresponding states.*"

§ 1. *The mean reduced surface of state for monatomic substances.* A difficulty which is by no means small is introduced into theoretical investigations dealing with the equation of state by the fact that, for every substance, and, in particular, for substances of simple molecular construction, the region that has been experimentally investigated extends over a small range of reduced pressure and of reduced temperature. If the law of corresponding states were strictly obeyed, this difficulty could be obviated by reducing and then combining with each other the regions investigated for the various substances. In this way the mean reduced equation of state has been synthesized in the form VII. 1 [1]). It has been obtained from AMAGAT'S observations on hydrogen, oxygen, and nitrogen, YOUNG'S on isopentane and AMAGAT'S and RAMSAY and YOUNG'S on ether. In this way the equation of state has been obtained for an imaginary substance which, if further amplified by the disturbance function [2]) for the neighbourhood of the critical point, is suitable for all calculations in which the validity of the law of corresponding states is assumed. And this equation is of particular use in tracing deviations from the law of corresponding states, for it affords a suitable means of easily comparing individual results, which cannot be satisfactorily represented by a special equation of state, with results obtained for other substances, and, particularly, with results obtained for those substances which have served for the calculation of equation VII. 1. When deviations of some particular substance from the imaginary substance in the same reduced state have been cal-

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1) Suppl. N⁰. 19 (May 1908).

2) Comm. N⁰. 104.

culated, then, the far more concise deviations from VII 1. may replace the actual results of the experiments themselves. Such deviations were determined for each of the substances used in the synthesis of equation VII. 1. with respect to whose reduced surfaces of state that of VII. 1. plays the part of a quasi-enveloping surface. The critical temperatures of the substances can greatly influence the differences existing between the separate surfaces; the peculiarities of the molecules, however, can influence them, too, in another way.

The object we had in view in our research upon the isotherms of monatomic substances was to obtain, in the same manner as that in which equation VII. 1. was obtained, a mean reduced equation of state in the synthesis of which observations on monatomic substances should exclusively be used. Unless in the structure of the various atoms of the monatomic substances further peculiarities are discovered which influence the equation of state, then, the only influence exerted upon the form of the reduced surface is that of the critical temperature. This influence will manifest itself in the deviations of the special equations from the mean equation undisturbed by other possible factors. And it is to be expected that the special surfaces of state for the various monatomic substances should systematically differ from the enveloping surface and from each other in such a manner that a gradual transformation would change the xenon [1]) surface into those for krypton, argon, and neon, to finally assume a limiting shape in the case of helium [2]). From the sequel, in which is given a first, but very small, step in the desired direction, it is evident that the mean reduced equation of state for monatomic substances which we desire to obtain, and which we shall indicate by $\mathrm{VII}_{\mathrm{mon.}}$, will exhibit important characteristic differences from the general mean equation VII. 1.

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[1]) We shall, for the present, leave out of consideration substances of higher critical temperature.

[2]) It was remarked in 1881 that a separate equation of state would have to be applied to each group of substances having similar molecules. (H. KAMERLINGH ONNES. Verh. Kon. Akad. 1881, Arch. Neérl. 30, p. 101). The group of monatomic substances has been made a subject of special study from this point of view by H. HAPPEL, see Ann. d. Phys. (4). 13. 340. 1904.

§ 2. *Comparison of argon isotherms* [1]) *with those of isopentane* (YOUNG) [2]), *ether* (RAMSAY *and* YOUNG) [3]) *and carbon dioxide* (AMAGAT) [4]) *between the reduced temperatures* 1.0000 *and* 1.1323.

In order to obtain a systematic comparison from the point of view of the law of corresponding states between the results obtained for argon and those for other substances, we have in the manner indicated in § 1, calculated the differences between the observed data for the various substances and the values obtained from VII. 1 [5]). To begin with, the critical temperature and pressure already published [6]) were used in the calculation of the virial coefficients for argon according to VII. 1, and, with the aid of these coefficients, deviations from VII. 1 were obtained. It appeared to be most suitable to work with percentage deviations of pv from values of pv given by equation VII 1 [7]).

The virial coefficients are given in table I and the deviations in table II.

The deviations for isopentane, ether and carbon dioxide from VII. 1. were calculated a considerable time ago; they form part of an extensive research upon the differences between the empirical equations of state for these substances as expressed by their deviations from the general mean reduced equation, of which only a very small part has yet been published. From amongst these, deviations are taken which can be compared with the argon isotherms between —100° C. and the critical point, that is, those which lie in the same region of reduced temperature as the argon isotherms. The deviations for all four substances were then united

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[1]) Comm. N⁰. 118*b* and C. A. CROMMELIN. Thesis for the doctorate, Leiden, 1910.

[2]) S. YOUNG, Proc. phys. soc. London, 1894/95, p. 602.

[3]) W. RAMSAY and S. YOUNG Phil. Trans. 178. 57. 1887.

[4]) E. H. AMAGAT, Ann. de chim. e d. phys. (6) 29, June and Aug. 1893.

[5]) For a critical examination of the observations it is also very desirable to substitute deviations from VII. 1. for the actual observations so as to eliminate experimental error, and to reduce to one common substance the results obtained by different observers. Our results for argon were treated in this fashion before being placed upon the diagram.

[6]) Comm. N⁰. 115.

[7]) For the method by which these calculations are made, cf. Comm. N⁰. 71.

TABLE I.

Virial coefficients for argon according to VII. 1.

t	$B_A.10^3$	$C_A.10^6$	$D_A.10^{12}$	$E_A.10^{18}$	$F_A.10^{24}$
+ 20°.39 C.	— 0.61763	+ 2.21916	+ 4.32836	+ 7.6045	— 4.35430
0.00 C.	— 0.77633	+ 2.21208	+ 3.09635	+ 8.7321	— 4.98937
— 57.72 C.	— 1.30816	+ 2.40067	— 0.67139	+ 10.5255	— 5.02409
— 87.05 C.	— 1.66571	+ 2.73556	— 2.83014	+ 10.5566	— 3.93044
— 102.51 C.	— 1.89979	+ 3.04873	— 4.10121	+ 10.4013	— 3.10842
— 109.88 C.	— 2.02794	+ 3.25078	— 4.76310	+ 10.3251	— 2.69045
— 113.80 C.	— 2.10156	+ 3.37635	— 5.13599	+ 10.2947	— 2.47655
— 115.86 C.	— 2.14198	+ 3.44818	— 5.35020	+ 10.2837	— 2.35600
— 116.62 C.	— 2.15723	+ 3.47581	— 5.41531	+ 10.2806	— 2.31432
— 119.20 C.	— 2.21026	+ 3.57411	— 5.67996	+ 10.2759	— 2.17669
— 120.24 C.	— 2.23230	+ 3.61597	— 5.78950	+ 10.2764	— 2.12239
— 121.21 C.	— 2.25318	+ 3.65616	— 5.89340	+ 10.2783	— 2.07246
— 130.38 C.	— 2.46836	+ 4.10021	— 6.96374	+ 10.3966	— 1.66293
— 139.62 C.	— 2.72584	+ 4.69951	— 8.27734	+ 10.8045	— 1.42979
— 149.60 C.	— 3.06753	+ 5.59972	— 10.15136	+ 11.8440	— 1.53961

in one diagram in which the deviations were plotted as functions of *log* $\lambda \mathfrak{v}$ in which $\lambda = \frac{p_k v_k}{T_k}$ and $\mathfrak{v} = \frac{v}{v_k}$.

Hence, the critical volume does not appear in the expression $\lambda \mathfrak{v} = \frac{p_k}{T_k} v$; only the critical temperature and pressure are used in the calculation of $\lambda \mathfrak{v}$, while, when different substances are being compared with each other a single but undetermined value is ascribed to λ for all substances. This method which has already been adopted on former occasions [1]) has the great advantage that it is not necessary to use the critical magnitude which is most uncertain, viz. the critical volume, and only well defined magnitudes are employed. To make λ the same for all substances, although it varies distinctly for the various substances [2]), may well appear somewhat strange at first sight. The systematic deviations of the various equations from VII. 1 revealed in the different values of λ are not, however, the only systematic deviations to which expression will here be given. There is, therefore, no danger in uniting this one kind of deviation with the other ones in the common representation which we try to obtain for them. According to the method we followed it appears to be possible to unite all deviations from the law of corresponding states in a single representation as definite as can be desired for the present; but, of course, we do not mean to say that it might not be found more suitable in a more extended and more searching study of the deviations from the law of corresponding states to adopt a different method of summarising these deviations.

In order to be able to ascribe the same value to λ in every case, all the volumes must be expressed in the same unit. This was not the case with the observations which are now being dealt with, so that some reductions were found necessary. The volumes in the argon isotherms and in the carbon dioxide isotherms, viz v_A, are expressed in terms of the experimental normal volume, while those in the isopentane and ether isotherms, viz v_y, are expressed in terms of the number of cubic centimetres per gram of the substance. Since we wished to express $\lambda\mathfrak{v}$ in terms of the theoretical normal volume for all the substances we calculated its values according to the following expressions:

for argon and carbon dioxide: $\lambda\mathfrak{v} = \frac{p_k}{T_k A_{A0}} v_A$;

for isopentane and ether: $\lambda\mathfrak{v} = \frac{p_k \gamma}{T_k A_{A0}} v_y$ [3]).

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[1]) Comm. No. 71.

[2]) Suppl. No. 14.

[3]) Arch. néerl. (2) 6, 874. 1901, Comm. No. 74.

TABLE II.

Percentage deviations of pv_A from pv_A (C) of the general mean reduced equation VII. 1.

d_A 1)	O—C in %	d_A	O—C in %	d_A	O—C in %	d_A	O—C in %	d_A	O—C in %	d_A	O—C in %
+ 20°.39 C.		0°.00 C.		— 57°.72 C.		— 87°.05 C.		— 102°.51 C.		—109°.88 C.	
20.499	0.0	20.877	0.0	23.509	+0.1	25.152	+0.3	25.571	+0.5	26.242	+0.6
25.759	0.0	26.581	—0.1	[28.575	—0.2]	34.467	+0.1	35.077	+0.4	34.807	+0.8
32.590	0.0	32.302	—0.1	33.793	—0.2	55.822	—0.1	[47.893	+0.9]	65.142	+0.8
35.759	0.0	37.782	—0.2	48.116	—0.3	71.444	—0.2	[53.752	+0.9]	87.176	+0.8
47.319	0.0	51.840	—0.5	64.948	—0.4	94.625	—0.7	62.240	+0.4	102.76	+0.5
59.250	—0.1	65.325	—0.7	90.695	—0.9	119.84	—1.0	[69.954	+0.9]	125.56	+0.2
								84.002	+0.2	148.32	—0.2
								95.802	0.0	180.84	—1.0
								115.88	—0.4		
								135.65	—0.7		
								158.01	—1.2		
— 113°.80 C.		— 115°.86 C.		— 116°.62 C.		— 119°.20 C.		— 120°.24 C.		— 121°.21 C.	
67.078	+1.0	69.947	+1.1	26.480	+0.9	26.871	+1.0	72.627	+1.7	27.326	+1.1
88.889	+1.0	91.308	+1.2	34.939	+0.8	34.965	+1.2	82.816	+2.0	35.283	+1.3
106.68	+0.7	108.02	+0.9	68.630	+1.2	70.314	+1.4	99.246	+2.0	71.459	+1.8
129.17	+0.5	131.51	+0.6	90.563	+1.2	70 481	+1.0	118.51	+1.8	85.580	+2.0
152.71	0.0	155.12	+0.1	110.19	+0.9	83.257	+1.1	136.31	+1.7	100.33	+1.8
155.40	0.0	179.94	—0.5	133.69	+0.7	96.834	+1.5	165.79	+0.9	[123.85	+1.9]
182.13	—0.5	[183.35	+1.8]	159.71	+0.2	98.863	+1.0	206.57	+0.1	148.95	+1.6
184.82	—0.7	235.47	—1.7	161.75	0.0	124.97	+0.6	280.25	—0.7	170.05	+0.9
212.99	—1.1	319.52	—2.9	[186.15	—0.4]	[143.71	+0.9]	338.95	0.5	234.13	—0.2
				210.02	—0.9	156.36	—0.1			333.75	—0.1
				[260.61	—2 0]	[172.25	+0.6]				
				331.29	—2.8	222 69	—1.8				
						275.02	—2.8				
						336.89	—3.4				
— 130°.38 C.		— 139°.62 C.		— 149°.60 C.							
27.394	+1.7	28.122	+2.4	29.183	+3.8						
31.583	+1.2	35.573	+2.9	34.646	+4.4						
34.726	+2.0										
55.807	+2.9										
65.125	+3.2										
77.821	+4.2										
101.71	+3.3										

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1) d_A means the density, expressed in terms of the normal density.

In these expressions $A_{A_0} = \frac{1}{v_N}$ is the ratio of the experimental to the theoretical normal volume, and γ is the specific mass [1]) in grams per c.c at normal temperature and pressure.

Values of *log* $\lambda\mathfrak{v}$. were marked off as abscissae, and as ordinates values of the common logarithms of the reduced temperatures. Lines parallel to the *log* $\lambda\mathfrak{v}$ axis represent the course of the equation VII. 1, while deviations are marked off from these lines, (positive above, negative below) in such a way that a 1 % deviation corresponds to 5 mm. on the accompanying diagram. We shall call this method of exhibiting the deviations in a diagram "arranging according to *log* t the deviations expressed as functions of *log* $\lambda\mathfrak{v}$." From this drawing which, since it contains the deviations for the various substances at the different reduced temperatures (the observation temperatures of the isotherms), has been somewhat abridged, the deviations for each substance for successive values of *log* $\lambda\mathfrak{v}$ were now read off, and the values thus obtained were then graphed as functions of *log* t, arranged according to *log* $\lambda\mathfrak{v}$. By reading from the graphs thus deduced, the deviations for the various substances were brought to the same reduced temperature. For these reduced temperatures were chosen the temperatures of the argon isotherms, viz.

1.00816. for argon corresponding to —122°.21 C.
1.01460, „ „ „ „ —120°.24
1.02151, „ „ „ „ —119°.20
1.03863, „ „ „ „ —116°.62
1.04368, „ „ „ „ —115°.86
1.05735, „ „ „ „ —113°.80
1.08337, „ „ „ „ —109°.88
1.13229, „ „ „ „ —102°.51

And finally, the deviations were graphed as functions of *log* $\lambda\mathfrak{v}$, and all reduced to the same temperatures. This diagram is reproduced on the Plate accompanying this Communication. The deviation curves for the reduced temperatures 1 01460 and

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[1]) In all these considerations we may neglect the difference between the specific mass and the density (number of grams pro m. L.).

1.04368 could not be drawn on it, as in order to do this distinctly the scale would have to be made too great. The rectangle on the right hand lower portion of the diagram borders the immediate neighbourhood of the critical state. It is best, while employing this method of critically examining the deviations, to leave this region out of account provisionally, as otherwise one would have to allow for the influence of the disturbance function [1]). A description of the information afforded by this plate concerning the deviations of the various substances seems to us unnecessary; it speaks for itself, and gives clear expression to the systematic deviations of argon from the other substances in this region.

§ 3. *Calculation of certain data which are of importance in the discussion of deviations from the law of corresponding states.*

To get an idea of deviations from the law of corresponding states, certain data are usually calculated, and we are now able to obtain their values for argon from our former experiments [2]).

a. By substituting values of argon vapour pressures in the well known VAN DER WAALS vapour pressure equation [3]):

$$\log \frac{p}{p_k} = f \frac{T - T_k}{T}$$

and using common logarithms we get the following values for f:

t	p in atm.	f
—140°.80 C.	22.185	2.415
—134°.72 C.	29.264	2.421
—129°.83 C.	35.846	2.457
—125°.49 C.	42.457	2.577

A cursory comparison of these values of f with those for other substances shows us that the value for argon is closer to the theoretical value of f at the critical point deduced from VAN DER WAALS's equation (1.737) than the values belonging to by far the greater number of other substances; this is what one would expect for monatomic substances. For carbon dioxide between —63° C. and the critical point f goes from 2.84 to 2.97 [1]; for isopentane [2] between 130° C. and the critical point f assumes a value between 2.75 and 2.95, while it further appears from the list published by KUENEN [3], that, with the exception of monatomic substances and a few others such as hydrogen, oxygen, and carbon monoxide, values of f are always still greater.

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[1]) Comm. No. 104.

[2]) Comm. No. 115; Comm. No. 118*a*; Comm. No. 118*b*.

[3]) J. D. VAN DER WAALS, Cont. I. p. 158.

b. From the critical data already published, and from the weight in grams of one litre of argon at normal temperature and pressure which, according to RAMSAY and TRAVERS [4] is 1.782, we found for the critical virial quotient

$$K_4 = \frac{RT_k}{p_k v_k} = 3.283.$$

This value is also closer to the theoretical value deduced from VAN DER WAALS's equation, 2.67, than those of almost all other substances, as is evident from the table of values given by KUENEN [5]. Hence, D. BERTHELOT's [6] estimate is probably much too low.

c. Let us write the equation of the rectilinear diameter of CAILLETET and MATHIAS [7] in the form

$$\frac{\rho_{\text{liq}} + \rho_{\text{vap}}}{2} = \rho_k - \alpha (T_k - T),$$

in which ρ_{liq}, ρ_{vap} and ρ_k are the liquid, vapour and critical densities in terms of the density of water of 4° C. respectively and α is the slope of the diameter; calling

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[1] J. P. KUENEN, Die Zustandsgleichung, p. 101, supplemented by KEESOM's measurements, Comm. No. 88.

[2] S. YOUNG l. c.

[3] J. P. KUENEN, l. c. p. 142.

[4] W. RAMSAY and M. W. TRAVERS, Proc. R. S. 67. 329. 1900.

[5] J. P. KUENEN, Die Zustandsgleichung, p. 60

[6] D. BERTHELOT, Journ de phys. (3) 10. 611. 1901.

[7] L. CAILLETET and E. MATHIAS, Journ. d phys. (2). 5. 549. 1886.

$$a_M = -\alpha \frac{T_k}{\rho_k}$$

the reduced slope, we can, with the liquid densities published by Baly and Donnan 1). and the value of the critical density already published, deduce from the isotherms

$$\begin{aligned} \alpha &= -0.003050 \\ a_M &= 0.9027. \end{aligned}$$

The inclination of the diameter for argon is, therefore, unusually great — greater than has ever yet been found for any other substance since α for most substances lies between —0.0005 and —0.0023 2).

In connection with the foregoing, it is of interest to note that Young 3) discovered an intimate relationship for substances of higher critical temperature between the diameter's inclination and curvature and the values of the critical volume deduced from the law of the diameter. Representing the curved diameter by

$$\mathfrak{D} = \mathfrak{a}_d + \mathfrak{b}_d \mathfrak{t} + \mathfrak{c}_d \mathfrak{t}^2$$

in which

$$\mathfrak{D} = \frac{1}{2}\left(\frac{1}{\mathfrak{v}_{liq}} + \frac{1}{\mathfrak{v}_{vap}}\right),$$

then we obtain the following corresponding relations

$$\begin{array}{lll} -\mathfrak{b}_d < 0.93 & K_{4d} < 3.77 & \mathfrak{c}_d > 0 \\ -\mathfrak{b}_d = 0.93 & K_{4d} = 3.77 & \mathfrak{c}_d = 0 \\ -\mathfrak{b}_d > 0.93 & K_{4d} > 3.77 & \mathfrak{c}_d < 0. \end{array}$$

On a former occasion 4) the diameter was considered to be straight for argon, and the assumption wat then justified; we must, there-

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1) E. C. C. Baly and F. G. Donnan, Journ. chem. Soc 81. 911. 1902.

2) E. Mathias, Le point critique des corps purs, p. 9 and 10.

3) S. Young, Phil. Mag. (5). 50. 291. 1900.

4) Comm. No. 118*a*.

Erratum Communication N⁰. 120*a*.

p. 12 line 5 from the bottom: for wat read was.

fore put $\mathfrak{c}_d = 0$. But we have just found a value for K_4, and, since $K_4 = K_{4d}$ [1]) it follows that

$$K_{4d} = 3.283 \text{ and} - \mathfrak{b}_d = a_M = 0.9027.$$

From this we may conclude either that argon is an exception to YOUNG's rule, or, as is not impossible, that its diameter is somewhat curved, in which case it would belong to the first group given by YOUNG. An accurate experimental research upon the diameter for argon would probably lead to important results bearing not only upon this point, but also upon the question of the value of the critical density of argon.

For oxygen MATHIAS and KAMERLINGH ONNES [2]) found

$$-\mathfrak{b}_d = 0.813,\ K_{4d} = 3.346.\ \mathfrak{c}_d = 0.$$

It appears, therefore, as if values of K_{4d} in YOUNG's criterion become smaller and smaller the lower the critical temperature of the substance.

d. We can, in the meantime, say nothing definite about the function

$$\left(T\frac{\partial p}{\partial T} - p\right)v^2$$

investigated by REINGANUM [3]) and by VOGEL [4]). An investigation of this point is, however, in progress.

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[1]) The subscript *d* in K_{4d} is used to indicate the fact that the value of the critical volume with which this number is calculated has been obtained from the diameter. Although the value here given for the critical virial quotient has been obtained from a value of v_k calculated from the isotherms, we have, nevertheless, assumed that we may write $K_4 = K_{4d}$, seeing that probably the two values of v_k obtained by the two different methods differ but little from each other. (See Comm. No. 118*a*).

[2]) 1911. Comm No. 117.

[3]) M. REINGANUM, Diss. Göttingen 1899. Ann. d. Phys. (4). 18. 1008. 1905. Phys. Ztschr. 11. 735. 1910

[4]) G. VOGEL, Diss. Freiburg (Baden) 1910, Ztschr. f. phys. Chem. 73 429. 1910.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,

Director of the Laboratory.

No. 120b.

H. KAMERLINGH ONNES. "Further experiments with liquid helium. C. On the change of electric resistance of pure metals at very low temperatures etc. IV. The resistance of pure mercury at helium temperatures."

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam,* **28 April 1911**, p. 1479—1481).

EDUARD IJDO — PRINTER — LEIDEN.

H. KAMERLINGH ONNES. "*Further experiments with liquid helium. C. On the change of electric resistance of pure metals at very low temperatures etc.* IV. *The resistance of pure mercury at helium temperatures.*"

§ 1. *Introduction.* Since the appearance of the last Communication dealing with liquid helium temperatures (December 1910) liquid helium has been succesfully transferred from the apparatus in which it was liquefied to another vessel connected with it in which the measuring apparatus for the experiments could be immersed — in fact, to a *helium cryostat.* The arrangements adopted for this purpose which have been found to be quite reliable will be described in full detail in a subsequent Communication. In the meantime there is every reason for the publication of a preliminary note dealing only with the results of the first measurements made with this apparatus, in which I have once more obtained invaluable assistance from Dr. DORSMAN and Mr. G. HOLST. These results confirm and extend the conclusions drawn from the previous experiments upon the change with temperature of the resistance of metals. Moreover, it was in the first place shown that liquid helium is an excellent insulator, a fact which hat not hitherto been specifically etablished. This was of importance since the resistance measurements were made with naked wires, a method that is permissible only if the electrical conductivity of the liquid helium is inappreciable.

§ 2. *The resistance of gold at helium temperatures.* In the second place a link in the chain of reasoning which I adopted in § 3 of Communication N⁰. 119 B to show that the resistance of pure gold is already inappreciable at the boiling point of liquid helium has been put to the test by determining the resistance in liquid helium of the gold wire Au_{III} which was then estimated by extrapolation on the analogy of the platinum measurements. Within the limits of experimental error which are indeed greater for the present experiment than was the case for the others that value is now supported by direct measurement. The conclusion that the resistance of pure gold within the limits of accuracy experimentally obtainable vanishes at helium temperatures is hereby greatly strengthened.

§ 3. *The resistance of pure mercury.* The third most important determination was one of the resistance of mercury. In Communication No. 119 a formula was deduced for the resistance of solid mercury; this formula was based upon the idea of resistance vibrators, and a suitable frequency ν was ascribed to the vibrators which makes $\beta \nu = a = 30$ ($\beta =$ Planck's number $h/k = 4.864 \times 10^{-11}$). From this it was concluded:

1⁰. That the resistance of pure mercury would be found to be much smaller at the boiling point of helium than at hydrogen temperatures, although its accurate quantitative determination would still be obtainable by experiment; 2⁰. that the resistance at that stage would not yet be independent of the temperature, and 3⁰. that at very low temperatures such as could be obtained by helium evaporating under reduced pressure the resistance would, within the limits of experimental accuracy, become zero.

Experiment has completely confirmed this forecast. While the resistance at 13.°9 K is still 0.034 times the resistance of solid mercury extrapolated to 0°C., at 4°.3 K it is only 0.00225, while at 3° K it falls to less than 0.0001.

The fact, experimentally established, that a pure metal can be brought to such a condition that its electrical resistance becomes zero, or at least differs inappreciably from that value, is certainly of itself of the highest importance. The confirmation of my forecast [1]) of this behaviour affords strong support to the opinion to which I had been led that the resistance of pure metals (at least of platinum, gold, mercury and such like) is a function of the Planck vibrators in a state of radiation equilibrium. (Such vibrators were applied by Einstein to the theory of the specific heats of solid substances, and by NERNST to the specific heats of gases).

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[1]) In connection with its deduction it is to be noted that the gold-silver thermo-element behaved in liquid helium quite so as the experiments in liquid hydrogen (Kamerlingh Onnes and Clay, Comm. No. 107*b*) made expect.

With regard to the value of the frequency of the resistance vibrators assumed before (one could try to obtain frequencies from resistances) it is certainly worth noting that the wave-length in vacuo which corresponds with the period of the mercury resistance vibrators is about 0.5 m.m. while RUBENS has just found that a mercury lamp emits vibrations of very long wave-length of about 0.3 m.m. In this way a connection is unexpectedly revealed between the change with temperature of the electrical resistance of metals and their long wave emission.

The results just given for the resistance of mercury are, since they are founded upon a single experiment, communicated with all reserve. While I hope to publish a more detailed description of the investigation which has led to these results in the near future, and while new experiments are being prepared, which will enable me to attain a greater degree of accuracy, it seemed to me desirable to indicate briefly the present position of the problem ^{1}).

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1) That this is justified is apparent from important papers which I have just received as this goes to press; in one NERNST extends the investigation referred to in Comm. No. 119 of the specific heats and is also independently led to assume a connection between the ernergy of vibrators and electrical resistance, and in the other this hypothesis is further developed by LINDEMANN.

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COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,
Director of the Laboratory.

Supplement No. 20

to No. 109—120.

JEAN BECQUEREL. „Contribution à la connaissance du phénomène de Zeeman dans les cristaux". *(With a plate)*.

(*Reprint from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam*, **26 Juni 1909**, pp. 146—150).

Eduard IJdo — Printer — Leiden.

JEAN BECQUEREL. „*Contribution à la connaissance du phénomène de* ZEEMAN *dans les cristaux*".

Au commencement de l'année dernière, nous avons observé, le Professeur KAMERLINGH ONNES et moi, divers phénomènes optiques et magnéto-optiques dans un certain nombre de cristaux de terres rares refroidis à la température de l'hydrogène liquide. Nous avons publié une première note [1]) indiquant seulement l'ensemble des effets observés; il reste à étudier en détail les clichés photographiques obtenus au laboratoire cryogène de l'Université de Leyde. Le Professeur KAMERLINGH ONNES a bien voulu me laisser le soin de ce travail, et je me propose d'indiquer dans une série de notes, au fur et à mesure de leur observation, les résultats que me fournira l'étude des clichés.

Les données que je présente ici forment une extension d'une note publiée à l'Académie des Sciences de Paris, où je m'étais borné à annoncer le résultat qualitatif sans donner les détails ni les mesures. Il s'agit du phénomène suivant; certaines bandes d'absorption de cristaux uniaxes se décomposent sous l'action d'un champ magnétique parallèle à l'axe optique et au faisceau lumineux en doublets dont les composantes ne peuvent être totalement supprimées par un analyseur circulaire convenablement orienté [2]).

Ce phénomène a été retrouvé par M. A. DUFOUR [3]) dans les spectres cannelés d'émission des chlorures et fluorures alcalino-terreux. M. DUFOUR a appelé "*résidus de polarisation*" les faibles bandes (*b b'* figure 1) qui dans les spectres juxtaposés de deux vibrations circulaires inverses paraissent prolonger les composantes *a a'*.

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[1]) JEAN BECQUEREL et H. KAMERLINGH ONNES. Comm. N⁰. 103; le Radium t. V. p. 235.

[2]) JEAN BECQUEREL. Comptes rendus t. 145 p. 413 (19 août 1907); le Radium t. V. p. 9. — JEAN BECQUEREL et H. KAMERLINGH ONNES loc. cit. § 9.

[3]) A. DUFOUR. Comptes rendus t. 146 p. 118 (18 janv. 1908) et p. 229 (3 février); le Radium t. V. p. 305.

Je ne crois pas exagéré de dire que parmi les manifestations variées du phénomène de Zeeman, cet effet est l'un des plus inattendus et des plus importants. La considération de la symétrie du champ, envisagée seule, permet bien, suivant une remarque due à M. Lorentz [1]) et récemment rappelée par M Cotton [2]), l'existence d'une polarisation incomplète de la lumière dans le champ magnétique; mais il n'en est pas moins vrai que, suivant les théories jusqu' à présent données (Lorentz, Voigt, Ritz . . .) un tel phénomène est peu probable dans le cas d'un cristal.

J'ai pensé qu'il n'y avait pas lieu de mettre en échec toutes les théories et que les faibles bandes (*b b'* figure 1) dont la superposition avec les composantes principales donne une lumière incomplètement polarisée sont en réalité, *non pas des résidus de polarisation de ces composantes principales, mais de nouvelles composantes* absolument distinctes de ces dernières : l'ensemble forme alors un quadruplet composé de deux doublets différents polarisés en des sens opposés. L'expérience a justifié cette manière de voir.

J'ai examiné les clichés que nous avons obtenus, le Professeur Kamerlingh Onnes et moi, et j'ai constaté que la raie 625$\mu\mu$ de la *tysonite*, sur laquelle j'avais observé pour la première fois l'effet en question, donne en réalité un *quadruplet formé par deux doublets polarisés en des sens opposés* ; grâce à la finesse de cette bande à 20° K. on voit (figures 1 et 2) que les résidus formant un doublet de 0$\mu\mu$,34 dans un champ de 15800 gauss sont nettement en dehors du doublet de 0$\mu\mu$,29 formé par les composantes principales : les deux doublets paraissent avoir même milieu

Sur les clichés de Leyde, il est facile de voir que pour les bandes 487$\mu\mu$,7 ; 642$\mu\mu$,3 ; 643$\mu\mu$,4 ; 645$\mu\mu$,6 ; 655$\mu\mu$,9 du *xénotime, les résidus n'occupent pas la même position que les composantes.* Pour la bande positive [3]) 522$\mu\mu$,15 du *xénotime*, particulièrement intéressante par sa finesse et sa grande sensibilité, il m'a semblé voir un décalage entre les composantes et les résidus.

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[1]) H. A. Lorentz. Rapp. au Congrès International de Physique (1900), t III p. 6.

[2]) Voir résumé des Communications de la Soc. franc. de Phys. Séance du 7 mai 1909.

[3]) Je désigne par *bandes negatives* les bandes donnant l'effet attribué à des charges négatives et par *bandes positives* celles qui donnent l'effet de sens contraire. Cette dénomination s'impose d'après le langage depuis très longtemps employé pour la polarisation rotatoire magnétique, puisqu'elle est en conformité avec le sens de la rotation au milieu des bandes.

J'ai alors repris à Paris les expériences, en refroidissant les cristaux avec de l'azote liquide (80° K.). J'ai ajouté aux pièces polaires habituelles d'un petit électro-aimant WEISS des pièces auxiliaires percées de trous de $1^{mm},5$. M. REGNIER ayant réussi à réduire à 4^{mm} la largeur de la partie rétrécie du tube de DEWAR, j'ai pu rapprocher les pôles de manière à atteindre un champ voisin de 25000 gauss

Dans les champs faibles (fig. 3 et 4) on constate d'abord que les deux résidus, pour la bande $522^{\mu\mu},1$ sont très dissymétriques, le résidu côté violet étant le plus intense alors que les deux composantes ont sensiblement la même intensité ; ce fait montre déja une certaine indépendance des prétendus résidus vis à vis des composantes. Au fur et à mesure que le champ croit, le résidu côté violet augmente d'intensité aux dépens de l'autre, et à partir de 20000 gauss on le voit bien nettement décalé à l'intérieur du doublet des composantes principales (figures 5 et 6). Pour 24000 gauss, le décalage est de $0^{\mu\mu},06$.

Des effets de même nature sont visibles pour de nombreuses bandes ; le tableau sur la page suivante résume quelques observations relatives au xénotime, faites avec une lame de $0^{mm},8$ d'épaisseur.

Un fait intéressant est le suivant : pour certaines bandes ($642^{\mu\mu},3$; $643^{\mu\mu},4$) le milieu du doublet faible est décalé par rapport au milieu du doublet principal. Il est possible que le doublet faible soit produit par une bande satellite très voisine de la bande principale, mais il se peut aussi que les deux doublets proviennent de la même bande, l'un au moins d'entre eux ayant une dissymétrie de position par rapport à la bande primitive[1])

L'expérience montre donc que les doublets à polarisation incomplète sont en réalité des quadruplets (ou peut-être même des types plus compliqués) formés de deux doublets (ou de deux parties) dont les polarisations sont de sens contraires.

Pour les bandes étudiées, les positions relatives des composantes semblent indépendantes de la température entre 80° K. et 14° K.

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[1]) J'ai d'ailleurs observé, pour les composantes principales, des dissymétries de position qui feront l'objet d'un travail ultérieur.

XÉNOTIME.

Longueur d'onde du milieu de la bande (mesurée à 80° Kelvin).	Sens de l'effet **Zeeman** pour le doublet principal.	Intensité du champ magnétique	Température de l'observation.	Largeur du doublet principal.	Positions relatives du doublet principal et du doublet secondaire.	
					Composantes déplacées vers les λ décroissantes.	Composantes déplacées vers les λ croissantes.
487$^{\mu\mu}$,7 (forte bande)	Phénomène positif	16700 gauss	20° kelvin	0$^{\mu\mu}$,18	pas de décalage appréciable entre la comp. principale et la composante secondaire.	Comp. secondaire décalée de 0$^{\mu\mu}$,04 à 0$^{\mu\mu}$,06 en dehors du doublet principal
522$^{\mu\mu}$,1 (fine, et intense)	" "	24300 "	80° "	0$^{\mu\mu}$,58	décalage de la comp. second. de 0$^{\mu\mu}$,05 à 0$^{\mu\mu}$,06 en dedans du doublet principal.	Comp. second. cesse d'être appréciable dans un champ intense.
523$^{\mu\mu}$,00 (fine et très faible)	" négatif	24300 "	80° "	0$^{\mu\mu}$,24	Compos. principale très faible.	Comp. principale plus intense que la bande primitive. Comp. second. en dedans du doublet principal : décalage de l'ordre de 0$^{\mu\mu}$,01.
525$^{\mu\mu}$,2 (fine, assez intense)	" "	24300 "	80° "	0$^{\mu\mu}$,31	Comp. second. en dehors du doubl. principal 0$^{\mu\mu}$,02 à 0$^{\mu\mu}$,03.	Compos. second. à peine visible.
642$^{\mu\mu}$,3 (intensité moyenne)	" "	16700 "	14° "	0$^{\mu\mu}$,56	Comp. second. en dehors du doublet principal 0$^{\mu\mu}$,06.	Comp. second. tres faible en dedans du doublet principal.
643$^{\mu\mu}$,4 (intensité moyenne)	" "	16700 "	14° "	0$^{\mu\mu}$,54	Comp. second. en dehors du doublet principal 0$^{\mu\mu}$,11.	Comp. second. à peine perceptible.
646$^{\mu\mu}$,6 (faible)	" "	16700 "	14° "	0$^{\mu\mu}$,60	Comp. second. en dehors du doubl. princ. 0$^{\mu\mu}$,02 à 0$^{\mu\mu}$,03.	Comp. second. en dehors du doublet principal 0$^{\mu\mu}$,02 à 0$^{\mu\mu}$,03.
654$^{\mu\mu}$,2 (Intense, assez fine)	" positif	22000 "	80° "	0$^{\mu\mu}$,25	Comp. second. en dehors du doubl. princ. 0$^{\mu\mu}$,03 à 0$^{\mu\mu}$,05.	Comp. second. pas nettement visible.
655$^{\mu\mu}$,9 (extrêmement fine)	" négatif	16700 "	14° "	0$^{\mu\mu}$,18	Comp. second. en dehors du doubl. princ. 0$^{\mu\mu}$,02 à 0$^{\mu\mu}$,03.	Comp. princip. très faible, comp. secondaire invisible.

On peut remarquer qu' à certains points de vue les deux groupes inversement polarisés sont liés : ils occupent des positions extrêmement voisines ; ils possèdent des écartements presque égaux ; ils paraissent enfin subir tous deux, sous l'influence des variations de température, les mêmes changements d'intensité que la bande primitive. Ils sont, au contraire, indépendants au point de vue des dissymétries d' intensité et de position.

Ces résultats, bien entendu, ne sont établis que pour les bandes des cristaux. Pour les spectres cannelés d'émission des vapeurs, étudiés par M. Dufour, je ne puis dire si les effets sont identiquement les mêmes, cependant je pense que les résidus ne doivent être qu'une apparence. Il y aura certainement une grande difficulté expérimentale à observer dans les vapeurs un décalage entre les composantes principales et les résidus ; il faudrait en effet des champs magnétiques dépassant 100.000 gauss pour pouvoir atteindre des écartements de doublets comparables à ceux que l'on réalise pour certaines bandes de cristaux avec moins de 25000 gauss ; de plus l'aspect dissymétrique des bandes des vapeurs est une grande gêne pour l'observation.

D'ailleurs, il est fort possible que les deux doublets polarisés en des sens opposés aient quelquefois la même position ; ce ne serait qu'un cas particulier du phénomène.

La conclusion sera la suivante :

Il existe des bandes qui donnent *à la fois* l'effet Zeeman négatif et l'effet positif, un même système vibrant se décomposant, sous l'action du champ, en deux parties liées entre elles, mais distinctes et différentes par le sens de leur polarisation circulaire.

Toute extension des anciennes théories ou toute théorie nouvelle du phénomène de Zeeman devra nécessairement rendre compte de ce fait. Il est à peine besoin de remarquer qu'on y parviendrait aisément, dans toutes les théories actuelles, en supposant que des électrons négatifs et des électrons positifs contribuent à la fois à former les bandes en question.

Je ne veux pas manquer, en terminant, d'adresser l'expression de ma plus vive gratitude à M. le Prof. Kamerlingh Onnes qui a bien voulu collaborer avec moi pour l'obtention des clichés qui ont été l'origine de ces observations. Je tiens aussi à remercier M. Ivan Werlein, l'habile constructeur qui a taillé avec une adresse remarquable les lames cristallines, et M. Matout, assistant au Muséum dont le concours m'a été précieux.

LÉGENDE DES FIGURES.

Figure 2. Bande $625^{\mu\mu},0$ de la tysonite, décomposée par un champ magnétique de 15800 gauss. Température 20° K. Spectres juxtaposés de 2 vibrations circulaires inverses.

On constate l'existence de deux systèmes polarisés en des sens opposés ; le doublet faible (secondaire) est plus écarté que le doublet intense (doublet principal).

Figures 3 à 6. Groupe vert du xénotime à 80° K. Aspects successifs des spectres juxtaposés de deux vibrations circulaires inverses, dans un champ progressivement croissant : fig. 3 $H = 6900$ gauss ; fig. 4 $H = 13700$ g. ; fig. 5 $H = 22000$ g. ; fig. 6 $H = 24300$ g.

Suivre en particulier la bande $522^{\mu\mu},15$. Fig. 3, on voit les 2 composantes principales prolongées par des composantes secondaires faibles, la composante secondaire étant un peu plus intense du côté violet que du côté rouge.

Fig. 4. La dissymétrie d'intensité des composantes secondaires s'accentue.

Fig. 5. La composante secondaire côté violet est nettement décalée en dedans du doublet principal.

Fig. 6. Le décalage s'accentue du côté violet. La composante secondaire côté rouge n'est plus visible.

(Ne pas confondre les composantes de la bande $522^{\mu\mu},15$ avec les composantes de la bande faible voisine $522^{\mu\mu},6$).

JEAN BECQUEREL. „Contribution à la connaissance du phénomène de Zeeman dans les cristaux.”

Fig. 1.

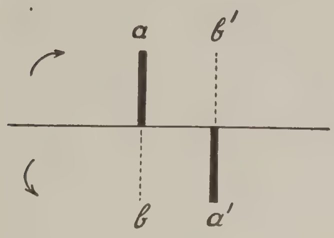


Fig. 1′.

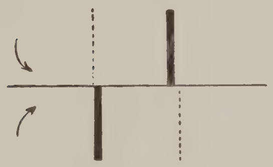


Fig. 2.

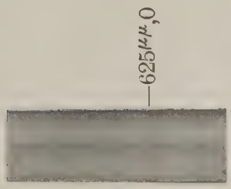


Fig. 3.

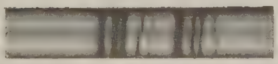


Fig. 4.

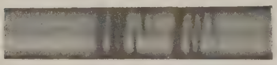


Fig. 5.

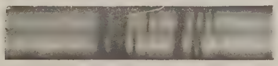
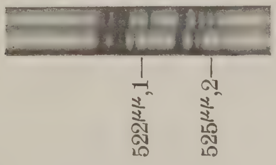


Fig. 6.



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Scientists who are interested in this matter may have photographic reproductions of the original spectrograms on application to the Director of the Laboratory.

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